Responses to Reviews

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Following evaluation of the re-submitted manuscript 6th Aug 2015

Authors response to Interactive comment on “Effects of global change during the 21st century on the nitrogen cycle”by D. Fowler et al.

The authors would like to thank the reviewers for the time spent reviewing the revised manuscript.

Please find below in black the reviewer comments and in BLUE the authors responses.

1). Page 38 section 7, a citation to Su et al. (2011) is missing in the main text (now only appears in the reference list).

Reference to Su et al (2011) inserted in text

2). Section 2.1, I am glad that the authors have implemented my suggestions and included discussions about the role of cryptogamic covers. It would be appropriate to cite not only Porada et al. 2014 but also Elbert et al. 2012 with regard to global terrestrial nitrogen fixation by lichens, bryophytes and other cryptogams, because Elbert et al. first addressed the issue and introduced the referenced carbon-scaling approach based on measurement data while Porada et al. later followed up with a model study.

Reference to Elbert et al (2014) added as suggested.

In addition an additional address has been added to the manuscript for Simpson, at his request.

Effects of global change during the 21st century on the nitrogen cycle

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Commented [MKE1]: See page 15 - there is a new subheading here but level is not clear - should it be 2.3 or 2.2.4? Title is: Global chnages in natural BNF 2010 to 2100. Check with David and then edit contents page here and level indication in text on page 15.

Abstract

The global nitrogen (N) cycle at the beginning of the 21st century has been shown to be strongly influenced by the inputs of reactive nitrogen (N_r) from human activities, including combustion related NO_x, industrial and agricultural N fixation, estimated to be 210 Tg N yr^{-1}in 2010 which is approximately equal to the sum of biological N fixation in unmanaged terrestrial and marine ecosystems. According to current projections, changes in climate and land use during the 21st century will increase both biological and anthropogenic fixation, bringing the total to approximately 600 Tg N yr^{-1} by around 2100. The fraction contributed directly by human activities is unlikely to increase substantially if increases in nitrogen use efficiency in agriculture are achieved and control measures on combustion related emissions implemented.

Some N cycling processes emerge as particularly sensitive to climate change. One of the largest responses to climate in the processing of N_r is the emission to the atmosphere of NH_3, which is estimated to increase from 65 Tg N yr^{-1} in 2008 to 93 Tg N yr^{-1} in 2100 assuming a change in global surface temperature of 5°C in the absence of increased anthropogenic activity. With changes in emissions in response to increased demand for animal products the combined effect would be to increase NH_3 emissions to132 Tg N yr^{-1}. Another major change is the effect of climate changes on aerosol composition and specifically the increased sublimation of NH_4NO_3 close to the ground to form HNO_3 and NH_3 in a warmer climate which deposit more rapidly to terrestrial surfaces than aerosols. . Inorganic aerosols over the polluted regions especially in Europe and North America were dominated by $(NH_4)_2SO_4$ in the 1970s to 1980s, and large reductions in emissions of SO_2 have removed most of the SO_4^{2-} from the atmosphere in these regions. Inorganic aerosols from anthropogenic emissions are now dominated by NH_4NO_3, a volatile aerosol which contributes substantially to PM_{10} and human health effects globally as well as eutrophication and climate effects. The volatility of NH_4NO_3 and rapid dry deposition of the vapour phase dissociation products, HNO_3 and NH_3, is estimated to be reducing the transport distances, deposition footprints and inter-country exchange of N_r in these regions.

There have been important policy initiatives on components of the global N cycle. These have been regional or country-based and have delivered substantial reductions of inputs of N_r to sensitive soils, waters and the atmosphere. To date there have been no attempts to devlop a global strategy to regulate human inputs to the nitrogen cycle. However, considering the magnitude of global N_r use, potential future increases, and the very large leakage of N_r in many forms to soils, waters and the atmosphere, international action is required. Current legislation will not deliver the scale of reductions globally for recovery from the effects of N_r deposition on sensitive ecosystems, or a decline in N_2O emissions to the global atmosphere. Such changes would require substantial improvements in nitrogen use efficiency across the global economy combined with optimisation of transport and food consumption patterns. This would allow reductions in N_r use, inputs to the atmosphere and deposition to sensitive ecosystems. Such changes would offer substantial economic and environmental co-benefits which could help motivate the necessary actions.

1 INTRODUCTION

While nitrogen is abundant, comprising 80% of the atmosphere, its form, as molecular nitrogen N_2 is largely unavailable to biota. Specialized organisms are able to fix nitrogen and transform it into compounds available for synthesis amino acids and other metabolic products. Before human activities contributed to nitrogen fixation, the global nitrogen cycling in soils, vegetation the atmosphere and oceans relied entirely on microbial biological fixation, plus a small contribution fron lightning. Human activities began to substantially contribute to the global nitrogen cycle at the beginning of the 20th century through combustion, which creates fixed nitrogen as NO_x, industrial NH_3 production (by the Haber-Bosch process) and by growing nitrogen fixing crops. The global nitrogen (N) cycle has been perturbed by human activity over the last 100 years with approximately two thirds of the annual flux of reactive nitrogen (N_r, which includes all compounds of nitrogen following fixation of molecular nitrogen N_2), entering the atmosphere at the beginning of the 21st century being anthropogenic in origin (Galloway et al., 2004, Fowler et al., 2013). This has led to widespread negative consequences through directly contributing to radiative forcing of climate, reductions in biodiversity at regional scales in terrestrial ecosystems and in damage to human health through aerosols and ozone production (Erisman et al., 2013, Sutton et al., 2011). Human modification of the N cycle also has substantial benefits, through sustaining the food supply to a global human population of seven billion and stimulating global CO_2 sequestration by terrestrial and marine ecosystems (Zaehle, 2013; Sutton et al., 2013b).

The damage by N_r to ecosystems, human health and climate result from leakage of N compounds from its use in agriculture, industry and transport (Erisman et al., 2013). A particular feature of the N cycle is the combination of the large number of forms, both oxidised and reduced, in which N_r exists, with biological and chemical transformations allowing the same emitted molecule of N_r to take part in a series of effects, both negative and positive, before being transformed back to molecular nitrogen and returned to the atmospheric reservoir. This has been termed the nitrogen cascade (Galloway et al., 2003) and substantially complicates an assessment of the pathways and effects of N_r in the environment.

The negative effects of human N fixation, are substantial and have been estimated to be 70-320 billion Euros annually for Europe (Sutton et al., 2011; Brink et al., 2011). A comprehensive global assessment of the costs of human use of fixed N has yet to be made. However, the scale of European use, at ~17 Tg N annually, represents only 8% of the total anthropogenic N_r fixed annually (210 Tg N yr^{-1}). As the local hot spots of N_r use in North America and especially in East and South Asia, show values of emission and deposition similar to or larger than in Europe, it is likely that the global costs of human use of N_r are therefore an order of magnitude greater than those for Europe. This would be consistent with a preliminary estimate of global damage costs associated with N pollution of 800 (200-2000) billion US dollars per year (Sutton et al., 2013b).

Recent analyses of the global N cycle have focussed on the magnitude of current fluxes (Fowler et al., 2013), effects of human activity on the processes and effects on human health, climate and ecosystems, especially in the regional assessments in Europe (Sutton et al. 2011, 2013b) and in the United States of America (Davidson et al., 2012;). The extensive conversions of N_r in the environment mediated by biological and chemical processes are sensitive to environmental conditions and thus are likely to respond to changes in climate over coming decades. Thus the current global N cycle is likely to change, regardless of future changes in human activities or human intervention to regulate losses to the environment.

The likely responses of the exchanges of N_r between and within the major global reservoirs in coming decades to changes in climate and land use have not been considered to date, and are the focus of this review.

Recent assessments of state of scientific understanding include 14 papers published by The Royal Society on the global nitrogen cycle (Phil. Trans. R.Soc.B368 2013). These relatively short papers focus on components of the global nitrogen cycle in the atmosphere, terrestrial marine and Polar Regions, and include a global overview (Fowler et al 2013). The coverage is not encyclopaedic and the main focus is on terrestrial ecosystems and the atmosphere. The effects of climate changes in the 21st century are not treated in detail within these papers.

The potential impacts of changes in climate and land use on the global nitrogen cycle are considerable in both the range and magnitude of effects. The processes which regulate transfers between the atmosphere and terrestrial and marine reservoirs are generally sensitive to aspects of climate that are expected to change, including temperature, absolute humidity and precipitation (Sutton et al., 2013b). Many of the major transfers are mediated by biological processes, especially microbiological transformations, which are very sensitive to changes in climate. The exchange fluxes of N_r compounds at the Earth's surface, including emission and deposition, are regulated by a combination of atmospheric transfer and surface reactions and biological regulation through stomatal exchange and soil microbiology. These processes therefore include physical, chemical and biological interactions combining to regulate the overall process. Most of the components of the pathway are sensitive to climate, and while the response of some components to specific changes in the environment may be predicted, the overall process relies on measurements to constrain the potential range of effects (Fowler et al., 2009; Monks et al., 2009).

Some of the effects appear straightforward, such as increases in emission fluxes of nitric oxide (NO) from soils and ammonia (NH_3) from vegetation with temperature, but when the full range of expected changes in climate and the number and phase in which the N_r compounds reside are included, the responses become complex and harder to quantify. To consider the whole N cycle and interactions with climate and land use change requires a coupled global climate and N cycle model, which to date has not been achieved. While parts of the biogeochemistry have been incorporated in global climate models, especially those linked to ozone chemistry and emissions of oxidised N (Stevenson et al., 2006), many of the interactions of reduced nitrogen compounds have yet to be included (Sutton et al., 2013b). In the absence of global modelling needed to quantify the interactions there have been a number of model investigations at regional scales. There have also been modelling studies of interactions between the carbon and N cycles which provide useful insight to biogeochemical interactions (Zaehle et al., 2013).

This paper explores current knowledge of the sensitivity of biological nitrogen fixation, emissions, atmospheric processing and removal of N_r compounds to changes in climate and land use, defined here as:

(a) *Climate change:* This refers to the change of the primarily environmental drivers temperature and rainfall (amount, frequency, seasonal distribution), both affecting soil environmental conditions but also site and landscape hydrology, vegetation cover and substrate supply. Land use is also influenced, since farmers will adapt land use and land management as climate changes (Kicklighter et al., 2014).

(b) *Land use change*: This refers to changes in vegetation cover, land use and management resulting in changes in substrate supply to the soil microbial community, but also triggers changes in soil and catchment hydrology. Policy and economic drivers also influence the uptake of measures aimed at promoting mitigation in the agricultural sector (MacLeod et al., 2010).

(c) *Atmospheric composition change*: This is mainly due to rising CO_2 concentrations, resulting in reductions in plant transpiration and increasing levels of soil moisture (e.g. Long et al., 2004), but also to changes in regional O_3 concentrations - affecting plant performance and, thus, e.g. plant litter production or transpiration – and / or atmospheric deposition of reactive nitrogen (Sutton et al., 2011), which is not only an additional Nr source for soil microbial processes but also drives forest C sequestration and changes in soil C and N stocks (De Vries et al., 2014).

The focus is on responses of the flow of nitrogen through terrestrial and marine ecosystems and the atmosphere to changes this century and includes new modelling and analysis as well as the published literature. Consequences for human health, ecosystems and food production of these likely responses are briefly considered.

The structure of the review follows the pathway from fixation of atmospheric nitrogen, by both biological and industrial processes to emission of gaseous N_r compounds into the atmosphe and removal by dry and wet deposition Interactions between global nitrogen and carbon cycles are included as they represent key areas of development of Earth system models and are a focus of wider academic interest in the global nitrogen cycle.

Some components of the nitrogen cycle are well supported by recent literature and extensive measurements, as in the case of surface-atmosphere exchange processes, and oxidized nitrogen compounds in the atmosphere, while others are poorly supported by measurements and recent research. This variability in knowledge leads to different approaches in the sections of the paper, concentrating on those components which have been subject to recent publications, or new modelling, specifically developed for this paper.

The review concludes with a brief discussion of the policy implications of climate-nitrogen cycle interactions, as this an important driver of the research agenda and provides context, and has been the subject of several recent publications (Sutton et al., 2011 and Sutton et al., 2013a).

2 BIOLOGICAL NITROGEN FIXATION

Biological nitrogen fixation (BNF) is currently estimated to provide a global annual input of 273 Tg N yr^{-1} to the biosphere (Fowler et al 2013) making it the largest single global input of N$_r$, although there are significant uncertainties about the magnitude and spatial distribution of fluxes (Fig. 1). If we assume that the global N cycle was in an approximate equilibrium prior to industrialisation, BNF would have been balanced by the reductive processes of denitrification returning molecular nitrogen (N_2) to the atmosphere, with estimates of around 260 Tg N yr^{-1} arising from terrestrial and oceanic sources (Galloway et al., 2004). The process of fixation is undertaken by a very limited range of highly specialised microorganisms that share an ability to use the nitrogenase enzyme to split the triple bond present in atmospheric N_2 and combine it with hydrogen to produce a source of N$_r$. Although the process is highly energy demanding, it is performed at ambient temperature and pressure unlike the industrial Haber-Bosch process that requires the reactants to be combined in the presence of an iron catalyst at between 300-500ºC in a reaction vessel at 20 MPa. Two main groups of organisms are responsible; free-living bacteria and algae (which are widespread in fresh water, oceans and uncultivated soils and often form mutualistic associations with a range of plant species) and symbiotic bacteria (mostly belonging to the genus *Rhizobium*) which form symbiotic associations with the roots of plants (mostly belonging to the family *Leguminosae*).

2.1 Terrestrial nitrogen fixation

In terrestrial environments, a wide diversity of both symbiotic and free-living N fixers contribute to BNF in non agricultural soils, but a lack of measurements results in large uncertainties in reported values. A meta-analysis of published data compiled from a large number of individual measurements of N fixation carried out in diverse ecosystems reported an average annual global flux of 195 Tg N with a range of 100-290 (Cleveland et al., 1999), although this was later revised down to 128 Tg (Galloway et al., 2004). It is thought that tropical environments are particularly important in contributing to terrestrial BNF, although these areas are associated with the least measurements. Recent measurements of BNF by methanotrophs in pristine peatland at high latitude by Vile et al. (2014) suggest appreciable fixation in these environments which have not been included in global estimates to date. Using net carbon uptake methods, Porada et al. (2014) and Elbert et al (2014) also suggest significant contributions to global nitrogen fixation from lichens and bryophytes.

Using an N balance approach in which the global N cycle is assumed to be in steady state, BNF can be estimated as the difference between inputs and outputs of N within a global context. This approach has suggested that preindustrial terrestrial BNF in natural ecosystems was only 44 Tg N yr^{-1} (Vitousek et al., 2013), however, such a small value questions whether current rates of natural BNF reported by Cleveland and others from up-scaling may have been overestimated. The recent estimate of BNF in natural terrestrial ecosystems of 58 Tg N annually by Vitousek et al. (2013) is substantially smaller than other recent syntheses of the literature, which are generally in excess of 100 Tg N annually. The most recent measurements of BNF in peatlands, which, although representing 3% of the world’s land surface, contain approximately 25% of the world's soil carbon, suggest an additional source in these regions in the range of 4.8 to 62.3 kg N ha^{-1} annually and a mean value of 25.8 kg N ha^{-1} annually (Vile et al., 2014). Net carbon uptake by lichens and bryophytes has also been used to estimate nitrogen requirement and indirectly nitrogen fixation by Porada et al. (2014), also suggesting a significant contribution to global N fixation by these plant communities. Given these new measurement-based values for extensive ecosystems, the value for global BNF in natural ecosystems seems unlikely to be smaller than 100 Tg N annually and the value proposed by Galloway et al. (2004) of 128 Tg N yr^{-1} is used here for 2010.

Biological N fixation provides a largeinput of fixed N to agricultural systems. Prior to the development of synthetic fertilizers at the beginning of the 20th century, most of the N used to produce crops and livestock would have been derived from this source. The current input is estimated to be approximately 60 Tg N yr^{-1}, taken as the central value in the range 50-70 Tg yr^{-1} from Herridge et al. (2008). This value is divided mainly between the grain legumes (peas and beans) and forage legumes (such as clover and alfalfa) contributing 21 and 19 Tg yr^{-1} respectively (Herridge et al., 2008). Estimates of BNF by the grain legumes are generally considered to be more reliable than those from forage crops since comprehensive records of the former are maintained by FAO (FAO, 2012). Other minor inputs of N by BNF in agriculture include symbiotic N fixation from tropical savannas used for grazing (14 Tg) free living micro-organisms associated with rice paddies (5 Tg), and sugar cane (0.5 Tg).

During the 20th century, there has been a rapid growth in the cultivation of leguminous crops contributing to an increase in associated BNF (Galloway et al., 2004). Future growth of legume crops will be constrained by the land area available to agriculture, and increases in production are most likely to occur when legumes are grown in place of other species. Emissions of nitrous oxide (N_2O) resulting from the growth of legume crops is generally smallby comparison with other crops, and the IPCC guidelines on greenhouse gas reporting assumes that the N input resulting from legume production is not associated with any N_2O emissions (IPCC, 2006). For this reason, increases in legume cultivation have been promoted as an opportunity to reduce N_2O emissions from agricultural systems by reducing emission intensity of fixed N inputs to agricultural systems (Luscher et al., 2014). Legumes also continue to provide the main source of N input to low input agricultural systems and organic farming globally.

2.1.1 Effects of climate change on terrestrial biological nitrogen fixation (BNF)

Biological N fixation associated with non-agricultural ecosystems is susceptible to changes in environmental conditions. A framework for understanding the environmental controls determining the rates of BNF in the biosphere has been proposed in which there is a coupling between N, C and Phosphorus (P) cycling (Houlton et al., 2008; Vitousek et al., 2002). Free-living and symbiotic organisms with the potential to fix N are at a selective advantage in environments with low P availability, however, the high energy costs of BNF require adequate supplies of available fixed C. The temperature sensitivity of the nitrogenase enzyme responsible for the fixation process has been clearly demonstrated in a global meta-analysis of fixation rates across dominant terrestrial biomes; the optimal temperature for fixation was found to be 25.2°C with a very sharp decline in rates of fixation below 5°C and above 40°C

(Houlton et al., 2008). Projected global increases in temperature are therefore likely to be associated with increases in BNF, providing that sufficient water is available to maintain NPP. However, other environmental changes may counteract increases resulting from climate change. The process of BNF is often down regulated by the presence of fixed N. Agricultural experiments have consistently shown lower rates of fixation in the presence of high concentrations of soil mineral N and organic N inputs (Ledgard and Steele 1992). The biological responses to temperature are generally positive and Q_{10} values (defined as the response factor for a 10 degree C temperature change) are often in the range 1.5 to 3 for soil temperatures between 5°C and 25°C, outside which non-linearities are common. Taking a Q_{10} of 2 and temperature increases by 2100 of 4°C, which appear probable (IPCC, 2013), the natural, terrestrial BNF in 2100 is likely to be 170 Tg N annually.

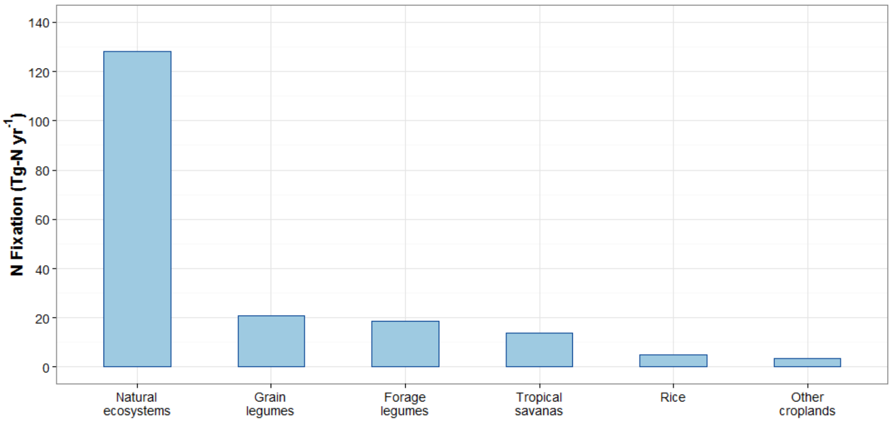

Figure 1: Summary of estimated global terrestrial contributions to biological N fixation in 2000. Values in Tg N yr^{-1} (based on Table 1 and activity projections).

Table 1: Global terrestrial contributions to biological N fixation in 2000. Values in Tg N per year with the range of estimates in brackets.

Agricultural system or ecosystem	Organism	Annual N fixation(T g yr^{-1}) and range	References
Grain legumes	Legume rhizobia	21 (10 – 21)	Herridge et al., 2008; Smil, 1999)
Forage legumes	Legume rhizobia	18.5 (12-25)	Herridge et al., 2008
Rice	Azolla	5 (4-6)	Herridge et al., 2008; Smil, 1999
Other croplands	Endophytic and free living bacteria	3.5	Herridge et al., 2008
Tropical savanas (used for agriculture)	Endophytic and free living bacteria	12 (5-42)	Cleveland et al., 1999; Herridge et al., 2008
Non agricultural ecosystems	Legume rhizobia and free living bacteria and algae	128 (44-290)	Cleveland et al., 1999; Galloway et al., 2004; Vitousek et al., 2013
Total		188 (77-387)	

2.2 Marine biological nitrogen fixation in the 21st century

Marine biological N fixation is performed by a diverse range of diazotrophs in plankton, microbial mat communities, sea grasses, coral reefs and sea sediments. Cyanobacteria of the genus *Trichodesmium* have been particularly well studied due to their prevalence and their formation of large blooms. Biological N fixation rates vary by species, and can be limited by temperature, light, oxygen, salinity, molybdenum, iron, and P..

Estimates have been made for global N fixation in the oceans, both by extrapolating from biological measurements, and by modelling the biogeochemistry. Recent reviews include Carpenter and Capone, 2008; Moore et al., 2013; and Voss et al., 2013.

Future changes to the ocean including increasing carbon dioxide (CO_2) concentrations, increasing stratification, and increasing temperatures, will likely result in an increase in marine nitrogen fixation. Nitrogen fixation leads to an increase in bioavailable N present in the form of ammonium and dissolved organic N (Mulholland et al., 2006). An increase in N_2 fixation would therefore lead to an increase in the amount of N_r available to enable further processes in the N cycle.

The objective of this section is to characterise the current state of knowledge on marine BNF, and the likely effects of changes in climate on marine BNFin the 21st century.

Light: Nitrogen fixers have strong preferences for specific light conditions. Depending upon the species, either light or darkness is required. Many non-heterocystous cyanobacteria fix nitrogen at night, however members of the genus *Trichodesmium* fix N only in the presence of light (Capone et al., 1997). *Trichodesmium* are therefore present at the surface of the ocean, and maximum fixation occurs at midday (Carpenter and Capone, 2008). Light sensitive diazotrophs like *Trichodesmium* could be affected by decreasing solar irradiance due to the presence of more clouds, resulting in a decrease in N_2 fixation.

Temperature: Enzyme activity generally increases with temperature, and this is true for nitrogen-fixing enzymes (nitrogenases). Staal et al. (2003) found that on short time scales, three strains of cyanobacteria exhibited a Q_{10} ranging from 1.08 to 4.72. *Trichodesmium* exhibited a Q_{10} of 1.12 for N_2 fixation in darkness from 20-35°C, and a Q_{10} of 2.06 from 15-20°C. In the presence of light, *Trichodesmium* exhibited a Q_{10} of 1.64 for 15-20°C, and 1.84 for 20-35°C. Fu et al. (2014) exposed strains of *Trichodesmium* and *Crocosphaera* to varying temperatures in the laboratory and found maximum N fixation to occur between 24-28°C and 28-30°C, respectively.

Increasing temperatures will likely cause the rate of N fixation to increase, both because enzyme activity increases at higher temperatures, and because the increase in sea surface temperatures will lead to an expansion of habitat suitable for diazotrophs (Hutchins et al., 2009). Boyd and Doney (2002) predict that habitat expansion will lead to an increase in N fixation of 27%.

Until recently, there was little evidence of marine diazotrophic activity in the cooler waters present at high latitudes (>50 degrees) (Carpenter and Capone, 2008). A recent study found substantial N fixation in the surface of the Canadian Arctic (Blais et al., 2012). These recent discoveries suggest diazotrophs may be fixing N in areas previously thought to be too cold for large levels of BNF.

Oxygen: Most nitrogen-fixing enzymes are inactivated by oxygen. Diazotrophs generally deal with this by performing N fixation either at night to avoid oxygen produced during photosynthesis, or within thick walled cells called heterocysts which maintain a localised anaerobic environment.

Nitrogen fixation has generally not been considered in oxygen minimum zone (OMZ) systems (Carpenter and Capone, 2008). Due to the removal of N_r by denitrification and anaerobic ammonium oxidation, OMZs have low concentrations of N_r relative to P (Canfield, 2006), and the conditions in these sites may be suitable for N fixation. Modelling efforts have considered N_2 fixation in OMZs (Canfield, 2006; Moore and Doney, 2007).

Expanding OMZs may increase areas conducive to denitrification and anaerobic ammonium oxidation. If nitrogen-fixing bacteria exist in balance with denitrification (Deutsch et al., 2007), then the increase in denitrification may lead to a corresponding increase in N_2 fixation. Oxygen minimum zones may also lead to an increase in the release of trace metals (Noble et al., 2012) and P from sediments, which could stimulate increased N_2 fixation.

Salinity: Diazotrophs may be able to live in a variety of saline conditions. For example, a *Trichodesmium* isolate was found to grow over a salinity range of 22-43 psu, but maximum growth and nitrogenase activity occurred over a narrow range of 33-37 psu (Fu and Bell, 2003). Changes in salinity are not expected to have a large effect on N fixation.

Trace metals and phosphorus: Nitrogenase requires both iron and molybdenum. Nitrogen fixation is limited by iron in approximately 35-75% of the oceans, globally (Moore et al., 2002; Berman-Frank et al., 2001). Molybdenum is generally not growth limiting (Paerl et al., 1987; Paulsen et al., 1991) as it is readily present in seawater. However, sulphate may inhibit the uptake of molybdenum, because sulphate is also present, and is stereochemically similar to molybdate (Howarth and Cole, 1985; Marino et al., 2003).

Phosphorus is an essential nutrient, however surface waters today are thought to be more limited by N rather than P over much of the oceans (Moore et al., 2007). Approximately 4% of the world oceans are limited by P (Moore et al., 2002).

Aeolian dust deposition leads to higher levels of iron reaching the subtropical North Atlantic Ocean. Under present day conditions, P may therefore be more limiting for diazotrophs in the North Atlantic, and iron may be more limiting in the North Pacific Ocean (Prospero and Lamb, 2003). Climate change may affect the transport of aeolian dust. If drier areas become drier, and/or wind speed increases, the amount of dust transported from continents to the oceans may increase, which would increase nitrogen fixation in areas limited by iron. However, if the areas that receive the dust are limited by other nutrients, then the increase in dust transport would have little effect.

Stratification: A strengthening of ocean stratification may lead to a decrease in nutrient upwelling, which would in turn lead to a shortage of N at the surface, which may cause an expansion of nitrogen-limited subtropical gyres (Sarmiento et al., 2004) and possibly encourage an increased rate of N fixation.

Carbon dioxide: Both model and laboratory studies of *Trichodesmium* isolates have shown an increase in N_2 fixation associated with increasing atmospheric CO_2 concentrations. Studies with *Trichodesmium* cultures have reported a range of measurements for the increase in N_2 fixation associated with increasing CO_2 concentrations from present day levels (375-380 ppm) to projected 2100 levels (~750-1000 ppm). Studies have reported an increase in rates of around 35-65% (Hutchins et al., 2007; Barcelos e Ramos et al., 2007; Kranz et al., 2009), and as high as 100-121% (Hutchins et al., 2007; Levitan et al., 2007). Barcelos e Ramos et al. (2007) predicted that N_2 fixation rates for *Trichodesmium* would increase by 50% from 60-85 Tg N yr^{-1} in 2005 to 90-128 Tg N yr^{-1} by year 2100 with projected increases in CO_2 concentrations under a business-as-usual emission scenario (scenario IS92a).

Hutchins et al. (2009) estimated that N_2 fixation by *Trichodesmium* alone will rise from present day levels of 60 Tg N yr^{-1} (Mahaffey et al., 2005) to 80-100 Tg N yr^{-1} by 2100, based on the response of a *Trichodesmium* isolate to increasing CO_2 levels. Hutchins et al. (2007) found that N_2 fixation rates for *Trichodesmium* levelled off at 1250 and 1500ppm, suggesting that N_2 fixation rates may stop increasing with increasing CO_2 levels by the year 2100.

Recent evidence indicates that unicellular cyanobacteria may fix at least as much N as *Trichodesmium* (Montoya et al., 2004). A laboratory study using the unicellular cyanobacterium *Crocosphaera watsonii* found that elevating CO_2 levels from 380ppm to 750ppm increased N_2 fixation rates by 40% (Fu et al., 2008), when not limited by iron. Based on measurements of the increase in N_2 fixation rates associated with CO_2 increases for seven strains of *Trichodesmium* and *Crocosphaera*, Hutchins et al. (2013) predict that over the next 100 years, N_2 fixation rates will increase by 4-23% for these seven strains. More evidence is needed to determine if other diazotrophs will be similarly affected by rising CO_2 concentrations. Barcelos e Ramos et al. (2007) predicted that N_2 fixation rates would increase by 50% by year 2100 with projected increases in CO_2 concentration.,

Anthropogenic N fertilization of the ocean leads to an increase in marine uptake of CO_2, however this may lead to an increase in N_2O emissions. Duce et al. (2008) applied Redfield stoichiometry to estimates of anthropogenic N_r deposition of 54 Tg N yr^{-1} and anthropogenic CO_2 uptake by the ocean of ~2.2 ± 0.5 Pg C yr^{-1} (IPCC, 2007), and calculated that the ocean may take up an additional 10% of atmospheric anthropogenic CO_2 as a result of atmospheric deposition of N_r. However, up to two-thirds of the decrease in radiative forcing generated by this drawdown of CO_2 may be offset by an increase in radiative forcing associated with an increase in the emissions of N_2O (Duce et al, 2008). A decrease in pH due to ocean acidification from rising CO_2 levels may lead to a decrease in the bioavailability of iron (Shi et al., 2010), which may in turn lead to a decrease in N_2 fixation for diazotrophs in areas where iron is limiting.

Table 2 provides a summary of the factors influencing marine N fixation, and the expected effects on marine BNF in the 21st century.

Table 2. Summary of future impacts of factors affecting marine nitrogen fixation.

Factor	**Effect on N_2 Fixation**
CO_2 increase (and decrease in pH)	+ 35% to 121% by 2100
Temperature increase leading to expansion of diazotroph habitat	+ 27%

Temperature increase leading to faster enzyme activity	+
Stratification leading to shortage of nutrients in surface waters	+
Dust containing iron	+ or -
Increase in oxygen minimum zones	+
Increase in nitrogen export from rivers	-
Increase in deposition of reactive nitrogen	-
Improved measurement methods	+
Phosphorus	Limiting nutrient

2.2.2 Present-day and pre-industrial estimates

Estimates of global ocean N_2 fixation (shown in Fig. 2) range from 75 to 200 Tg N yr^{-1} (Galloway et al., 2004; Carpenter and Capone, 2008; Moore et al., 2006; Deutsch et al., 2007; Eugster and Gruber, 2012; Luo et al., 2012), with recent estimates at around 130-140 Tg N yr^{-1} (Deutsch et al., 2007; Eugster and Gruber, 2012; Luo et al., 2012). Deutsch et al. (2007) estimated global ocean N fixation to be 140 Tg N yr^{-1}, using observed nutrient concentrations and an ocean circulation model. Eugster and Gruber (2012) used two methods to estimate the preindustrial global nitrogen fixation rate in the oceans to be 131 Tg N yr^{-1} (94, 175) and 134 Tg N yr^{-1} (117, 150), by combining geochemical observations with a two-dimensional box model. Deutsch et al. (2007) and Eugster and Gruber (2012) found that the rates of N_2 fixation were higher in the Pacific Ocean than the Atlantic. Luo et al. (2012) compiled a global database of diazotroph abundances and N_2 fixation rates, and estimated the global pelagic (open ocean) N_2 fixation rate to be 140 ± 9.2 Tg N yr^{-1} (arithmetic mean ± one standard error). One possible limitation of this approach is that 99% of the data were collected within the range of 40°S to 55°N, and if substantial N_2 fixation is found to occur outside of this range, it may be an underestimate. Luo et al. (2014) applied a multiple linear regression model to the same database of field observations and found an estimate of N_2 fixation of 74 (51–110) Tg N yr^{-1} for the open ocean.

Luo et al. (2012) note that the most common method for field measurements of N_2 fixation has recently been found to underestimate the rates for *Trichodesmium* by 62% (Großkopf et al., 2012). Extrapolating from the differences found between the $^{15}N_2$ tracer bubble-addition and dissolution methods, Großkopf et al. (2012) estimate that the global marine N fixation rate measured using the new method would be 177 ± 8 Tg N yr^{-1}.

Although recent midpoint estimates appear to have coalesced at around 130-140 Tg N yr^{-1}, there is still a great deal of uncertainty due to the large variance in measurements (Luo et al., 2012), and recent measurements of nitrogen fixation rates in areas not previously thought to have high levels of diazotrophy.

2.2.3 Effects of global change on marine biological nitrogen fixation

The most important effects will likely be due to temperature and increasing CO_2 concentrations. Marine BNF will increase from present day estimates of 140 (100-200) Tg N yr^{-1} to 166 (120-240) Tg N yr^{-1} due to temperature effects alone. Present day BNF estimates were scaled up using the Q_{10} of 1.64 for *Trichodesmium* (15-20°C) (Staal et al. 2003).

In addition to the factors discussed above, estimates of N fixation may increase in the future even if the actual rate remained constant. This is because the most common method for taking field measurements of marine N fixation has recently been found to underestimate the rate, so future estimates of N fixation may increase as the methods become more accurate (Großkopf et al., 2012). In addition, recent evidence suggests that regions such as coastal, aphotic, and arctic regions may exhibit more N_2 fixation that previously thought.

Taken together, the factors discussed above suggest that marine N fixation will increase in the future, which may lead to an increase in ocean drawdown of CO_2. Several feedbacks may offset this increase. Increasing rates of N_2 fixation may drive areas to P and iron limitation, thereby limiting ultimate N_2 fixation rates.

2.3 Global changes in natural BNF 2010 to 2100

It appears likely that global BNF will increase during this century in marine and terrestrial ecosystems. The total terrestrial natural N fixation by the end of this century suggested from these arguments is 170 Tg N annually, approximately 40% larger than the value at the beginning of the 20th century. Marine BNF is projected to increase from 120 TgN yr^{-1} to 166 TgN yr^{-1} by 2100 , an increase of 38% on the 2010 value.

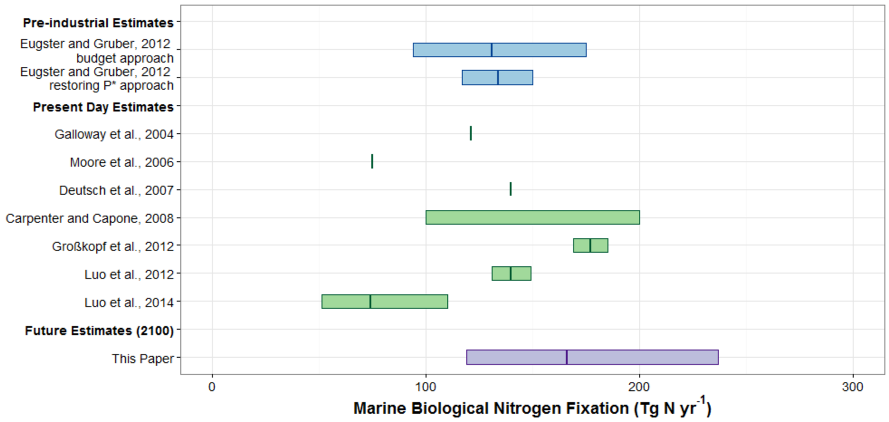

Figure 2: Summary of pre-industrial (blue), present (green), and future (purple) estimates of marine biological nitrogen fixation (BNF). Estimate from Carpenter and Capone (2008) represents their summary of the range presented in the literature, and includes no midpoint. Luo et al., 2012 values are arithmetic mean ± standard error,

so range limits may not be directly comparable to other estimate range limits. Estimates for fixation by *Trichodesmium* alone by Barcelos e Ramos et al. (2007) (60-85 Tg N yr^{-1} in 2005, 90-128 Tg N yr^{-1} by year 2100) and Hutchins et al. (2009) (80-100 Tg N yr^{-1} by 2100) are included in text but not presented in figure because the estimates in the figure are for total marine BNF.

3 ANTHROPOGENIC FIXATION OF NITROGEN IN THE 21ST CENTURY

Human demand for fixed N through the 21st century will be driven by requirements for food and industrial use. There is also unintended nitrogen fixation resulting from combustion related NO_x emissions. Set against these drivers for increased Nr fixation, control measures to mitigate emissions will regulate the net anthropogenic contribution to global nitrogen fixation.. A range of authors have considered the available scenarios and possible development trajectories including most recently Winiwarter et al. (2013) and Bouwman et al. (2013). The scenarios and time scales used by these authors differ, with Bouwman et al. (2013) projecting trends to 2050, rather than the end of the century. However, given the uncertainty in projections of this kind, they provide a useful guide for the likely trends. The projections from Winiwarter et al. (2013) are based on story lines and methodologies similar to those of the RCP (Representative Concentration Pathways) as used in the 2014 IPCC assessment of climate change through the 21st century. However, while based on the RCP scenarios, only the N_r from combustion is taken directly from the IPCC methods as N_r formation was not a focus of the scenario developments for the IPCC. Together with mineral fertilizer and industrial use of N_r, fixation is projected in the range 140 Tg N yr^{-1} to235 Tg N yr^{-1} by 2100, depending on the RCP chosen and compares with their estimate of 170 Tg N yr^{-1} in 2000. The year 2000 value is smaller than the estimate of 210 Tg N yr^{-1} by Fowler at al. (2013), but within the uncertainties shown in each synthesis. The projections from Winiwarter et al. (2013) imply modest overall change in N_r production by human activity through the 21st century as a consequence of gradual increases in efficiency compensating for increases in demand for fertilizer and industrial N_r applications, combined with reductions in nitrogen oxide (NO_x) emissions from combustion resulting from expected emission controls. Indeed, there have been important reductions in emissions of combustion N_r, as NO_x to the atmosphere throughout Europe, North America and other highly developed economies. Typically these have reduced NO_x emissions by about 50% over the last 30 years in these regions. Similar controls are likely for combustion emissions in the rapidly developing economies of Asia in the decades ahead. However, for reduced N, the global trend has been a monotonic increase in N_r fixation for most countries in the world outside Europe, and the social trends in rapidly developing economies towards increased meat consumption seem likely to continue the trend. Given these historical trends and the unwillingness of governments throughout the world to regulate the supply of reduced N_r for agriculture and industry, the assumption that N_r production will remain constant through the 21st century seems implausible.

A substantial increase in nitrogen use efficiency (NUE) seems likely, as has been achieved in European agriculture over the last 30 years, but this is unlikely to prevent a continued increase in global agricultural nitrogen use. Given that human N_r production doubled between 1980 and 2010, a period in which global population increased by 2.5 billion, and most projections show a similar population increase during the 21st century, the demand for food and other nitrogen consuming activities (transport, heating and consumer goods) will most likely lead to a substantial increase in industrial N fixation. Assuming NUE increases, it is possible that anthropogenic N fixation grows only by 30% between 2010 and 2100. This simplistic assumption would lead to 2100 N_r production through the Haber-Bosch process of 160 Tg-N yr^{-1} and total annual anthropogenic production Nr of 243 Tg N yr^{-1}.

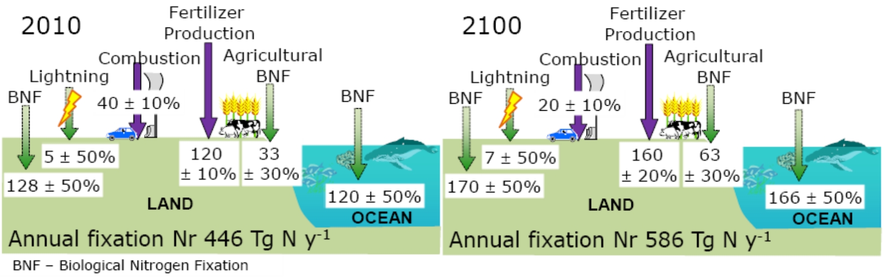

Figure 3: Global biological nitrogen fixation in natural ecosystems and by human activity in 2010 (left) and 2100 (right).

The global changes in fixation discussed above are summarised in Fig. 3, which show large increases in the total N fixed from 446 Tg N yr^{-1} in 2010 to 586 Tg N yr^{-1} in 2100 accompanied by substantial increases in the uncertainties of the component fluxes.

The N_r fixed by BNF and human activity is then used by and transformed within ecosystems and products of the chemical and biological processing cascade through terrestrial and marine ecosystems and the atmosphere. It is important now to consider the effect of changes in the environment this century on the fate of the N_r.

4 EFFECTS OF ENVIRONMENTAL CHANGES ON THE FATE OF N_r IN TERRESTRIAL AND MARINE ECOSYSTEMS

The total fixation of N through natural (BNF), combustion and Haber Bosch processes is projected to increase during the remainder of the 21st century, possibly to approximately 600 Tg N, an increase of 50% over values at the beginning of the century, (Fig. 3). The subsequent fate of the N_r in terrestrial and marine ecosystems and the responses of the different pools of N_r to changes in climate, and especially temperature are now considered for terrestrial and marine ecosystems.

The fixed N, whether by natural processes in soils and the oceans or by human activities is predominantly in the reduced form as ammonia (NH_3) or ammonium (NH_4^+) initially. Once formed, N_r is readily transformed in the environment and it is important to describe the likely effects of changes in the environment on the fate of N_r, and quantify, where possible the probable impacts due to climate and land use change, in short, which are the components of the N cycle that are most responsive to expected changes in climate and land use?

4.1 Terrestrial ecosystems: Emissions of NH_3 from terrestrial ecosystems through the 21st century

The global total emissions of NH_3 to the atmosphere at the beginning of the 21st century have been estimated by Sutton et al. (2013b), at 59.3 Tg N yr^{-1} of which 33 Tg N yr^{-1} is from livestock and crops. The N_r fixed industrially through NH_3 manufacture, mainly for fertilizers, is currently 120 Tg N yr^{-1}, thus the emissions to the atmosphere from livestock and crops represent roughly a quarter of the annual fertilizer production, effectively fertilizing the atmosphere. This, substantial quantity is the unintentional leakage of the N_r from farming systems due to the volatility of NH_3. Also presented in this analysis of global emissions of NH_3 are values for emissions from all other major sources. Given the spatial and temporal variability in emission rates and the sensitivity to climate, and especially temperature, the range of different emission estimates is small among the seven different estimates (35 to 65 Tg yr^{-1}) summarised, which reflects the fact that these estimates are not fully independent. It is suggested by Sutton et al. (2013b) that overall uncertainty is around ±30%, pointing to a range of emissions for 2008 of 46 Tg N yr^{-1} to 85 Tg N yr^{-1}.

The forces which have governed overall industrial production of fixed N have largely been economic, responding to the demand for food and the response functions between crop productivity and fertilizer use (Jensen et al., 2011) in which the economic benefits of increased yields have driven global N fertilizer use demand. At the same time, an increase in global meat consumption per capita (Erisman et al., 2008) has magnified fertilizer requirements and NH_3 emissions (Westhoek et al., 2014). This includes both the NH_3 emissions from fertilizer in growing animal feeds and the ammonia emissions from livestock manures, in animal houses, manure storage, land application and from grazing animals, where the used of housed livestock substantially increases emissions compared with pasture-only systems.

Global projections for future N_r use have not generally included possible control measures to reduce emissions of NH_3 to the atmosphere, which would increase the NUE. There are exceptions, in the case of the Netherlands and in Denmark, where policies to reduce the leakage of N_r to the environment led to substantial reductions in atmospheric emissions (EMEP, 2014). Although first NUE estimates have now been provided for each country in the world (Sutton et al., 2013a), it is a matter for ongoing and future analysis to show how these have evolved over time and to demonstrate the quantitative relationships between reduction between N emissions, including NH_3, and improvement of NUE. In the global projections of N_r use through the 21st century provided by both Erisman et al. (2008, using the SRES approach) and Winiwarter et al. (2013, using the RCP approach), scenarios included the potential to improve crop NUE, while Sutton et al. (2013a), examined the N savings possible also as a result of improving NUE across the full agri-food chain.

Global demand for food is likely to increase by 40% by 2050 due to population growth and a changing diet (Godfray et al., 2010), especially in the rapidly developing regions. The largest uncertainties in estimating future emissions of NH_3 to the atmosphere are the consumption drivers (food amount, food choice), the amounts of fertilizer and manure N applied and the effect of climate on the fraction emitted (van Vuuren et al., 2011a; and Sutton et al., 2013b, respectively). Excluding the climatic interaction (which is addressed below), emissions resulting from demand for food and industrial uses, have been estimated by van Vuuren et al. (2011a) to increase from 60 Tg N yr^{-1} in 2000 to between 70 and 80 Tg N yr^{-1} by 2100.

4.1.1 Effects of changes in climate on terrestrial emissions of NH_3

The processes of exchange of NH_3 between terrestrial ecosystems and the atmosphere have been subject to detailed field studies and intercomparisons of methods (Sutton et al., 1995, 1998, 2009; Flechard et al. 1999, 2013) and are discussed further in this review. The most recent estimates of the influence of climate change on emissions of NH_3 are by Sutton et al (2013b).

The surface atmosphere exchange of NH_3 is generally described numerically using a resistance analogy in which the vertical flux (F_t), is given by the potential difference between the surface and a reference height in the atmosphere divided by the sum of resistances in the pathway from the source to the reference height and comprising $R_a(z)$ and $R_{b,}$ the turbulent atmospheric and quasi-laminar boundary layer resistances respectively.

$$F_t = [\chi(z_{o'}) - \chi(z)] / [R_a(z) + R_b] \qquad \text{Equation (1)}$$

In most ecosystems, the concentration at the surface, ($\chi z_{o'}$) is non-zero, due to presence of NH_4^+ in the apoplast of vegetation. In these conditions the value of $\chi z_{o'}$ is proportional to a ratio $\Gamma=[NH_4^+]/[H^+]$ of the canopy/ground surface, where according to the thermodynamics:

$$\chi = 161500/T \exp^{(-10380/T)}[NH_4^+]/[H^+] \qquad \text{Equation (2)}$$

Temperatures (T) are in Kelvin and the scheme is represented schematically in Fig. 4.

The bi-directional exchange between surface and atmosphere of NH_3 modifies the spatial patterns of NH_3 fluxes in the landscape, with reduced emission or even deposition downwind of large sources (Fowler et al., 1998).Quantifying changes in NH_3 emission this century requires knowledge of apoplast and leaf litter NH_4^+ and pH, scaled through the coming decades over global vegetation. The data required to calculate net exchange fluxes in this way are not available. However, Sutton et al. (2013b) argue that by examining model ecosystems and their exchange of NH_3 a surrogate for the likely change may be seen in empirical data. When it comes to global upscaling of NH_3 emissions, this also needs to bear in mind that the wide range of different terrestrial NH_3 sources are likely to have differing temperature responses, due to the role of different interacting factors.

To illustrate these effects, a model ecosystem was used for which both a global modelling framework and field measurements are uniquely available, namely NH_3 emission from seabird colonies. In addition to the availability of measurements and modelling, they are also globally important sources of NH_3 and are distributed geographically across a broad range of climates, with minimal human intervention, so that the effects of climate differences can be assessed without confounding management interactions (Blackall et al., 2007; Riddick et al., 2012; Sutton et al., 2013b). This approach demonstrated a strong climate dependence in the ammonia emissions, with the modelling approach (incorporating Eq. (2)), agreeing closely with the measured datasets.

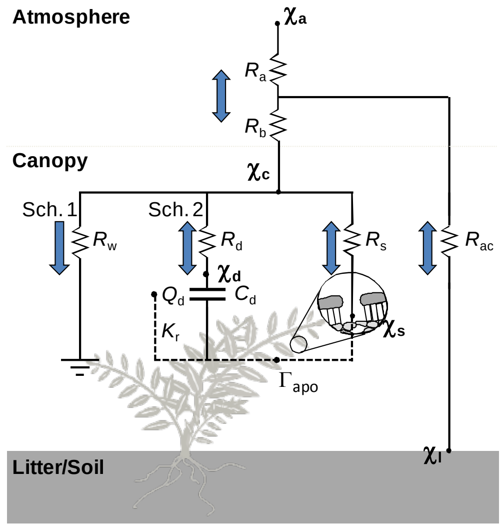

Figure 4: A resistance analogue of NH_3 exchange including cuticular, stomatal and pathways to soil (Sutton et al., 2013b). Two methods for cuticular exchange schemes are shown: 1, Steady-state uptake according to a varying cuticular resistance (R_w); 2, Dynamic exchange with a reservoir of NH_4^+ using a varying capacitance (C_d) and charge (Q_d). Within-canopy transfer (R_{ac}), cuticular adsorption/desorption (R_d) and stomatal exchange (R_s). Also shown are the air concentration (χ_a), cuticular concentration (χ_d), stomatal compensation point (χ_s), litter/soil surface concentration (χ_l) and the canopy compensation point (χ_c).

Combining all sources of NH_3 emission globally, studies provided the data to model likely responses of terrestrial NH_3 emissions to a 5 degree increase in global temperature and showed that emissions in 2008 of 65 Tg-NH_3-N (45-85), increased to 93 (64-125) Tg-NH_3-N in 2100 (Sutton et al., 2013b), based on anthropogenic activity levels for 2008. This may be compared with an estimated increase in NH_3 emissions based on increased anthropogenic activities (excluding the climatic response), and of no-change for natural sources, of 42% (33- 52%) increase by 2100. Combining the increases in anthropogenic activity expected up to 2100 according to the RCP8.5 (Lamarque et al., 2011), with the estimated effect of climate warming on emissions, gives an overall estimate of NH_3 emissions for 2100 of 132(89-179) Tg N yr^{-1}. As Sutton et al. (2013b, supplementary material) point out, this value is nearly a factor of three higher than that included in the currently mapped EDGAR database, which is a consequence of including: a) additional sources (including oceans, see further below), b) the effect of the climate change feedback and c) the anticipated increase in anthropogenic activities.

4.2 Ammonia exchange over the oceans in the 21st century

In marine ecosystems NH_3/NH_4^+ is produced by phytoplankton and other organisms. Although the aqueous-phase partitioning between NH_3 and its protonated form NH_4^+ is dominated by NH_4^+, the majority of emissions are in the form of NH_3. Ammonium is quickly assimilated by phytoplankton, so NH_3 and NH_4^+ are usually present in low concentrations in the surface ocean.

4.2.1 Factors affecting the flux of ammonia between the atmosphere and the ocean

The exchange of ammonia between the ocean and the atmosphere depends on several factors: the concentrations of ammonia in the surface layer of the ocean and in the boundary layer of the atmosphere, temperature, and wind speed (Johnson et al., 2008). The flux across the atmosphere-ocean interface can be described by (Liss and Slater, 1974):

$$F = k_g \{(NH_{3(g)}) - K_H \ [NH_{3(sw)}]\} \qquad \text{Equation (3)}$$

where F is the flux betweenthe atmosphere and the ocean (mol m^{-2} s^{-1}), k_g is the gas-phase transfer velocity (m s^{-1}), the NH_3 concentrations are given in mol m^{-3}, and K_H is the dimensionless Henry's Law coefficient for ammonia, $NH_{3(sw)}$ refers to surface water NH_3 concentration .

The Henry's law constant for ammonia can be calculated as follows (McKee, 2001):

$$K_H = (17.93\ (T/273.15)\ e^{(4092/T)-9.70})^{-1} \qquad \text{Equation (4)}$$

where T is temperature in Kelvin.

The concentration of NH_3 present in seawater depends on the partitioning between NH_3 and NH_4^+, which is affected by pH, salinity, and temperature. This dissociation can be described by the logarithmic acid dissociation constant, pKa (Bell et al., 2007):

$$pKa = 10.0423 - (0.0315536\ \ T) + (0.003071\ \ S) \qquad \text{Equation (5)}$$

where T is the temperature in °C, and S is salinity in g/kg. Chemical reactions and transport of NH_3 into the atmosphere (from terrestrial emissions) and the ocean (from biological activity, deposition and river export) also affect the levels of NH_3 present.

4.2.2 Flux estimates

The present-day direction of NH_3 flux is believed to be from the atmosphere to the oceans at high latitudes, where the oceans are colder, allowing more gases such as NH_3 to be dissolved. In contrast, the oceans are believed to be a source of NH_3 emissions at lower latitudes, where the oceans are warmer, promoting a greater partitioning to the gas phase (Eq. (4)) and Johnson et al., 2008). When considering the global oceans together, the net flux is believed to be a small emission from the oceans to the atmosphere (Bouwman et al., 1997; Dentener and Crutzen, 1994; Galloway et al., 2004).

Ocean-atmosphere NH_3 fluxes vary across regions and seasons, and observations are limited. As a result, there are only a few quantitative estimates of global flux, all of which are highly uncertain. Dentener and Crutzen (1994) estimated the flux to be 7.0 Tg N yr^{-1} from the oceans to the atmosphere. They did this by taking a distribution of dimethylsulphide (DMS) emissions modelled by Bates et al. (1987), and assuming equal molar emissions of NH_3 and DMS. Although both DMS and NH_3 are produced by phytoplankton, assuming an equal molar relationship is acknowledged by Dentener and Crutzen (1994) to be speculative. The relationship between NH_3 and DMS may have been tightly coupled under pre-industrial conditions, but this is unlikely to be true under the present strong anthropogenic influences on the N cycle (Johnson and Bell, 2008), especially in coastal waters.

An independent estimate of global ocean NH_3 emissions was provided by Bouwman et al., (1997) who applied an ocean carbon cycle model to calculate an NH_3 flux of 8.2 Tg N yr^{-1} for 1990. However, this did not account for non-zero atmospheric NH_3 concentrations, and Bouwman et al. (1997) acknowledged that doing so might reduce the net sea-atmosphere emission flux by a factor of two. For comparison, Galloway et al. (2004) estimated preindustrial, present, and future marine NH_3 emissions using a compensation point approach to be 5.6 Tg N yr^{-1}. However, it is unlikely that the flux would remain constant over these time periods, given the human perturbations to the N cycle.

Steadman et al. (in preparation), have improved these estimates by implementing the bi-directional flux calculation method described by Johnson et al. (2008), following Eqs. (3-5), accounting for both regional and temporal patterns in ocean and atmospheric concentrations of NH_3 and temperature. The flux is calculated by dividing the ocean surface into 5 degree grid squares, and determining the gas transfer velocity and the Henry's law constant for NH_3 within each grid square, using temperature, pH, and wind speed. The resulting estimated NH_3 flux for 2005 is 5.7 Tg N yr^{-1} from the ocean to the atmosphere. Atmospheric concentrations of NH_3 were obtained from STOCHEM (Lamarque et al., 2013; Derwent et al., 2003) model output. Surface ocean NH_3 and NH_4^+ concentrations were obtained from the British Oceanographic Data Centre.

These recent analyses suggest that the global NH_3 emission estimate of 8.2 Tg N yr^{-1} of Bouwman et al. (1997), which was incorporated into the global emissions estimates of Sutton et al. (2013b), summarised above, may be overestimated. If so, the estimates of Sutton et al. (2013b) should be reduced by around 2.5 Tg N yr^{-1} for 2008, giving total emissions of 63 (44-82) Tg N yr^{-1}, again based on ±30% uncertainty.

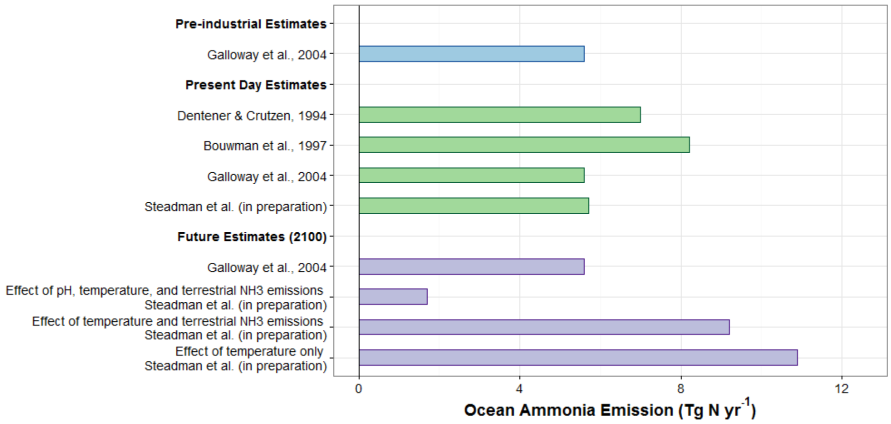

Figure 5: Summary of pre-industrial (blue), present (green), and future (purple, for 2100) estimates of marine ammonia flux from ocean to atmosphere.

4.2.3 Future impacts

The future ocean-atmosphere flux of NH_3 will be affected by increasing temperatures, increasing terrestrial NH_3 emissions, and ocean acidification from elevated CO_2 levels which lowers the pH of the water. The mechanism of both of these effects is an alteration of the partitioning of ammonia and ammonium in the ocean, as illustrated by Eq. (5). The lower pH results in a greater relative concentration of ammonium. The lower concentration of NH_3 will therefore result in lower emissions. Climate change and ocean acidification will also have indirect effects on ocean ecosystems, leading to changes in plankton populations and species composition.

The decreased marine emissions of NH_3 in the future, combined with increasing N deposition and export from rivers, suggest that the future oceans may accumulate more reactive N, leading to eutrophication and OMZs. Some of the additional N_r may result in an increase in denitrification and associated N_2O emissions.

The expected temperature and pH changes in the ocean associated with climate change and ocean acidification will likely have a large effect on the ammonia flux. Based on the estimates of Bouwman et al. (1997), Eq. (2) and a 5°C warming scenario, Sutton et al. (2013b, supplementary material) estimated that ocean NH_3 emissions would increase to 15 Tg N yr^{-1}. However, as noted above, the baseline may have been an overestimate, while the interaction with rising CO_2 levels was not included.

Preliminary model results suggest that after accounting for the increasing temperatures and terrestrial emissions associated with RCP8.5, and the expected ocean acidification (a decrease in mean surface ocean pH of 0.31, from 8.14 in 2000 to 7.83 in 2100 (IPCC, 2013)), the estimated future NH_3 flux for 2100 is 1.7 Tg N yr^{-1}. If temperature increases and increasing terrestrial ammonia emissions are accounted for, but ocean acidification neglected (the effect of pH is excluded), the estimated emission for 2100 would be 9.2 Tg N yr^{-1}. If atmospheric NH_3 concentrations and ocean pH were to remain at 2000 levels, but temperatures increase as expected under RCP8.5, the estimated 2100 ammonia emission is 10.9 Tg N yr^{-1}. Comparison of the bars in Fig. 5 shows that in relative terms the effect of ocean acidification is the largest driver, providing more than a factor of three difference in the flux calculated by Eq. (3).

4.3 Terrestrial emissions of nitric oxide and nitrous oxide

4.3.1 Global sources of NO and N_2O in the atmosphere

NO_x .Sources of atmospheric NO_x ($NO+NO_2$) are soils, natural fires, lightning, transport from the stratosphere and combustion of fossil fuels. The sinks are in both soil through microbial uptake and the atmosphere, through reactions with OH (Miyazaki et al., 2012; Logan et al., 1983. Global NO_x emissions have increased 3 to 6 fold since the industrial revolution due to increased fossil fuel and biomass burning (Prather and Ehhalt, 2001). Recent new estimates of global NO_x emissions based on a combination of a top down inventory based on satellite observations, and bottom-up inventory, have constrained the global emissions to 40 Tg N yr^{-1} (Jaeglé et al., 2005; Martin et al., 2003). Fuel combustion (fossil and biofuel) were the largest source, contributing 58% to the total budget, followed by soils (22%), biomass burning (14%), lightning (8%), stratospheric/tropospheric exchange (0.2%) and aircraft (0.1%) (Jaeglé et al., 2005; Martin et al., 2003). Largest soil contributions were from the African and Australian continents (39% of total), whereas in the more industrialised US and Europe soil emissions contributed only with 12 and 18% to total emissions respectively (Fig. 6). The monthly satellite NO_x data, links peak soil derived NO_x emissions with the onset of the rainy seasons in North equatorial Africa, and N fertilization of agricultural land in the northern and mid latitudes. These observations imply that the Yienger and Levy (1995) emission factors together with the Wang et al. (1998) algorithm for canopy exchange need to be revised upward substantially (Jaeglé et al., 2005).

Hudman et al. (2012) improved the presentation of soil NO_x emissions in global models by replacing the simple emission factors (Yienger and Levy, 1995) with equations representing spatial and temporal patterns of soil moisture, temperature, pulsing, fertilizer, manure and atmospheric N deposition and biome. The BDSNP model (Berkeley-Dalhousie Soil NO_x Parameterization) was coupled to a global chemistry-transport model GEOS-Chem, which normally used the Yienger and Levy (1995) (YL95) scheme for soil emissions (Wang et al., 1998), but retained the YL95 canopy reduction component. The new model calculated larger emissions for the below canopy emissions (10.7 Tg N yr^{-1}) relative to the YL95 approach (7.4 Tg N yr^{-1}). Total above canopy soil NO_x emissions were calculated at 9 Tg N yr^{-1}, in good agreement with the Jaeglé et al. (2005) study. The new model was validated using satellite nitrogen dioxide (NO_2) data provided by OMI (Ozone Monitoring Instrument, Hudman et al., 2010). Their model was able to reproduce the monsoon induced soil NO peak in North equatorial Africa and the interannual variability of soil NO_x fluxes over the Great Plains in the US.

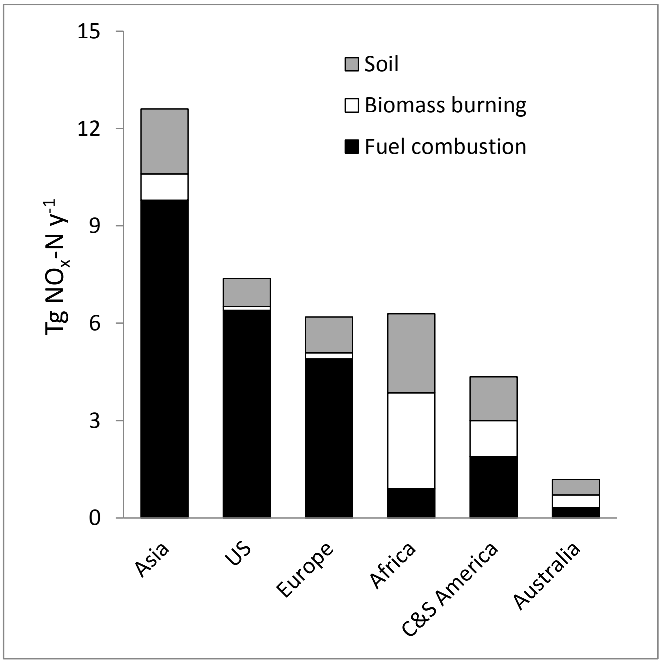

Figure 6: Spatial distribution of NO$_x$ emissions for the year 2000 from the main sources: Fossil & biofuel combustion, biomass burning and soils and main region. Data are the *a posterior* data (top down and bottom-up NO$_x$ emission inventory from Jaeglé et al. (2005).

N_2O: Nitrous oxide, a long-lived (114yr) greenhouse gas, contributing to 10% of the global radiative forcing (Denman et al., 2007), and in the stratosphere is now the main cause of stratospheric O_3 depletion (Ravishankara et al., 2009). Microbial denitrification and nitrification processes are responsible for 87% of the annual global N_2O budget (18.8 Tg N yr^{-1}; Syakila and Kroeze, 2011), with contributions from natural soils (35%), agriculture (27%) and oceans (25%). Non biological sources are responsible for the remaining 13% through fossil fuel combustion, biofuel and biomass burning and industrial processes. Atmospheric N_2O concentrations have been rising since the industrial revolution from 270 ppb to over 319 ppb. It has always been assumed that increased N fertilizer use is responsible for this rise. Recent measurements of isotopic N_2O composition ($^{14/15}$N) in the atmosphere are consistent with this assumption (Park et al., 2012), and N fertilized agricultural soils are responsible for almost 16% of global annual N_2O emissions. All agricultural activities are responsible for two-thirds of the total anthropogenic N_2O emissions (Davidson and Kanter, 2014), and more than one-third is associated with animal production.

Natural soil emissions are the largest single global source of N_2O, with largest emissions from the warm wet regions in the Amazon, South-East Asia and Africa. These are also the regions for which data coverage is poor relative to Europe and North America. Using an artificial neural network approach and available field observations Zhuang et al. (2012) calculated that 30% of the total natural soil contribution was from tropical evergreen broadleaved forests followed by 17% for woody savannas. Their total estimate for global soil emissions was 3.4, ranging from 2.0 – 4.6 Tg N yr^{-1} for the year 2000. This is lower than the range 6-7 Tg N yr^{-1} used by Syakila and Kroeze (2011), but with the very large uncertainties these values are probably not significantly different.

4.3.2 Soil processes responsible for NO and N_2O emissions

Denitrification: Denitrification is the major N loss pathway for N_r (Fig. 7). The ratio of the denitrification products N_2O and N_2 depends on localised environmental conditions in the soil. This microbial process, performed by archaea, bacteria or fungi, using oxidised nitrogen compounds such as nitrate or nitrite as an alternative electron acceptor in the absence of oxygen (Butterbach-Bahl et al., 2013), removes approximately 30-40% of N_r inputs to watersheds (Seitzinger et al., 2006).

Microbial denitrification is a highly spatially distributed process occurring in soils, sediments or water bodies if environmental conditions become unfavourable for aerobic degradation of organic matter. It mostly occurs at aerobic/anaerobic interfaces in soils, e.g. in riparian zones where lateral water flow from upstream regions provides a steady influx of nitrogen oxides as well as dissolved organic C to the waterlogged and oxygen (O_2) depleted soil zones in such topographic depressions. Thus, riparian areas are hotspots of denitrification (Pinay et al., 2007) as well as often hotspots of soil N_2O emissions (Jungkunst et al., 2008; Butterbach-Bahl and Dannenmann, 2011). Denitrification is a heterotrophic process in which nitrate (NO_3^-) is used as a terminal electron acceptor during the oxididation of C substrates (Groffman et al., 2006). Thus, at least three pre-conditions need to be fulfilled: a) oxygen depletion, b) availability of nitrogen oxides and c) availability of easily degradable C substrates. In wastewater denitrification is the key process removing NO_3^-, but it is also a major loss pathway of N fertilizers in agriculture. Loss rates of N_2O from fertilized cropland due to denitrification have been reported to be up to 240 kg N ha^{-1} yr^{-1} (Barton et al., 1999), thus, potentially even exceeding fertilizer application rates.

Denitrification is activated if soils become water-saturated or water-logged, e.g. due to heavy rainfall or irrigation. The sudden increase in soil moisture, blocking macro- and micropores with soil water, decreases O_2 diffusion into soil by approximately a factor of four. Since microbial metabolism as well as plant root respiration continues, the soil becomes anaerobic. Thus, besides being spatial highly distributed, with certain hotspots such as riparian areas in the landscape, denitrification is also temporally highly discontinuous and is a so-called "hot-moment" phenomenon (Groffman et al., 2006, 2009).

Nitrification: Biological and abiotic processes in soils are responsible for the production and consumption of NO and N_2O. Principal microbial processes leading to NO/N_2O production are nitrification and denitrification, and nitrifier denitrification (Fig. 7). There may be other theoretically feasible processes, which have not yet been identified in soils (Medinets et al., 2015; Schreiber et al., 2012). Chemodenitrification , the chemical decomposition of NO_2, is an important source of NO in acid soils and soils rich in humic acids (Stevenson et al.,1970; Zumft, 1997). Reduction of nitrite (NO_2^-) to NH_4^+ is also known to be a source of N_2O in some reduced environments (Fig. 7; Baggs, 2008)

Nitrification is the microbial oxidation of NH_4^+ to nitrate (NO_3^-), with hydroxylamine and NO_2^- as essential intermediates. This process occurs in all soils and aqueous systems and involves a wide range of microorganisms. In the denitrification pathway NO and N_2O are obligate intermediates; whereas in nitrification they are by-products and thought to operate when conditions are suboptimal for further oxidation to NO_3^- (Conrad et al., 1996; Baggs, 2008). Both processes take place in the same soil microsites, but even with modern technologies such as isotopic labelling, use of microelectrodes and molecular analysis, it is difficult to unravel the detailed biological pathways responsible for NO and N_2O production under different conditions (Schreiber et al., 2012). Generally, NO emissions are considered to be associated with nitrification conditions and N_2O emissions with denitrification conditions.

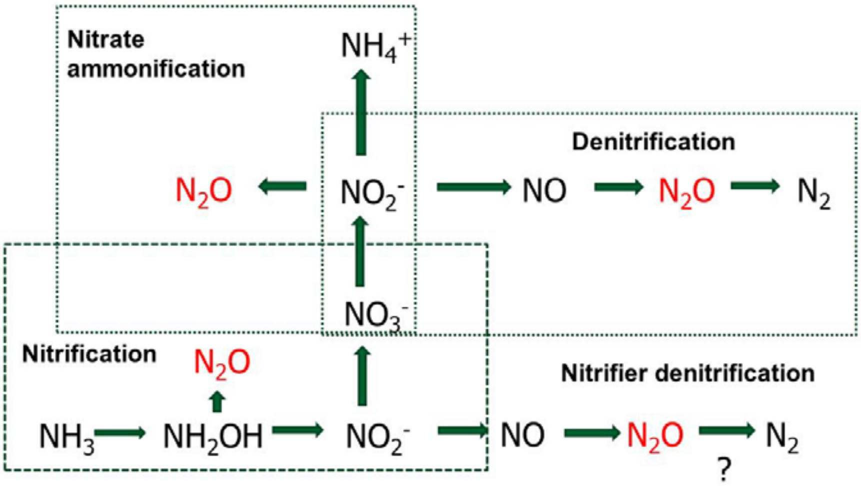

Figure 7: A schematic diagram of the microbial processes contributing to N_2O production (adapted from Baggs, 2008).

4.3.3 Effects of climate change on NO and N_2O emissions

Climate change: Microbial activity will increase with temperature if the process itself is not limited by the availability and supply of the respective substrate(s), such as easily degradable C and oxidised N compounds. If global and regional temperatures continue to increase, there is a potential for denitrification and nitrification rates also to increase. The study by Luo et al. (2014), for example, shows that in grassland soils undergoing experimental warming of 2°C over a period of 10 years, key metabolic pathways related to C and N turnover accelerated. In the case of denitrification, this increase was 12%. However, if summer temperatures increase whilst summer rainfall decreases, denitrification rates would decrease substantially, since the most important environmental precondition for denitrification, anaerobic conditions are not provided. These conditions would however be favourable for NO and N_2O emissions via nitrification.

An additional consequence of rising temperature will be increased rates of transpiration and evaporation (Long et al., 2004). In conclusion, it can be assumed, that changes in soil moisture as driven by changes in rainfall patterns and amounts and evapotranspiration fluxes will very likely dominate the overall response and overwhelm any direct temperature effects on denitrification, nitrification and NO and N_2O emissions. Moreover, expected changes in the hydrological cycle at regional to continental scales will affect not only the seasonality of soil moisture changes, catchment and watershed hydrology, and the size and temporal expansion and shrinking of riparian zones (Pinay et al., 2007). Thus, when considering climate change effects on NO and N_2O emissions one must include changes in rainfall (amount, frequency and seasonality), evapotranspiration and associated changes in surface and subsurface water flows and catchment/watershed hydrology in the focus (Butterbach-Bahl and Dannenmann, 2011).

Land use: Expected changes in climate are already triggering changes in land use and land management. The area of irrigated agricultural land is expanding quickly not only in semi-arid but also in humid temperate climates to adapt agriculture to predicted temporal water scarcity due to climate change (Trost et al., 2013). Reviewing the existing literature on irrigation effects on soil N_2O emissions Trost et al. (2013) found that in most cases irrigation increased N_2O emissions in a range from +50 to +150%, which is very likely caused by increased denitrification activity in such soils. Irrigation may increase (Liu et al., 2010) or reduce NO emissions (Abalos et al., 2013), depending on the wetness of the soil.

The large scale introduction of no-till agriculture, especially in Latin America (Abdalla et al, 2013), may affect N_2O and NO emissions. A study by Rosa et al. (2014) which addresses denitrification activity in no-till production systems in the Argentinian pampas, suggests that increased soil aggregate stability in no-till systems, and its effects on C sequestration, water infiltration, soil aeration and microbial habitat provision, is the most important factor for explaining changes in denitrification activity, rather than by changes of the microbial community (Attard et al., 2011). For a cereal field in Scotland, UK no-till increased N_2O emissions, but decreased NO emissions, whereas tillage had the opposite effect and increased NO but decreased N_2O emissions (Skiba et al., 2002).

Atmospheric composition change: The main component is the increasing concentration of atmospheric CO_2, and in some regions increasing levels of tropospheric O_3, and atmospheric deposition of N_r. Increasing levels of atmospheric CO_2 increases water use efficiency of plant photosynthesis, resulting in increased soil moisture levels and hence increased N_2O emissions by denitrification or nitrification, (e.g. Kammann et al., 2008), but probably reduced NO emissions. Also rhizodeposition of easily degradable C compounds has been shown to increase (Singh et al., 2010) as a result of additional inputs of N_r to soil by atmospheric deposition, i.e. the other denitrification substrate besides labile organic C compounds, the overall effect of atmospheric composition change on denitrification should be to increase denitrification.

To predict quantitatively how climate change will influence terrestrial denitrification and nitrification rates and associated NO and N_2O emissions it is necessary to know both the quantities of N_r used by agriculture and the effects of climate on the soil processing. The balance of evidence suggests a net increase of NO and N_2O emissions due to the increases in N_r use to need to feed a growing population and increased demand for biofuels. For N_2O IPCC (2013) climate simulations, using a new set of scenarios (representative concentration scenarios RCP2.6, RCP4.5, RCP6 and RCP8.50), suggests an average increase of N_2O by 1.6 Tg N_2O-N (range -1.4 to 4.5 Tg N_2O-N) between 2010 and 2050. A similar increase in the remaining half of the 21st century would lead to an increase in emissions by 28% over the century to 3.2 Tg N yr^{-1} in 2100. An increase in soil NO emissions during the 21st century of similar magnitude to those for N_2O seem likely , as emissions of both gases are primarily driven by agricultural and biofuel production. This would lead to soil emissions of NO in 2100 of 11.5 Tg N yr^{-1}.

It is clear that predicted changes in rainfall and regional hydrological cycles are more important than direct effects of temperature for large scale denitrification activity. Increases in precipitation at higher latitudes appear common to many climate model projections for the later decades of this century (IPCC, 2013), but the variability in magnitude and distribution precludes clear regional quantification. Likewise the drying of the Mediterranean basin is a common feature in some climate model simulations. Such a response would decrease N_2O emissions, but could increase NO emissions. These expected changes are overlaid by changes in land use and land management, which are also partly triggered by climate change. Moreover, changes in atmospheric composition are indirectly feeding back on denitrification activity in soils too, e.g. by affecting plant performance and thus, nutrient and water flows. To better understand climate change effects on regional and global denitrification and nitrification activities multi-factorial climate (e.g. Mikkelsen et al., 2008) and land use/ land management change experiments are needed. Such studies have still only been run for relatively short term, which hampers the detection of interactive and nonlinear effects, or the identification of thresholds and tipping points (Luo et al., 2011).

5 ATMOSPHERIC PROCESSING - CHEMISTRY

Higher temperatures increase the rates of almost all chemical conversions: the higher kinetic energies associated with warmer temperatures means reactions proceed faster. Temperature has particularly important effects on two equilibria involving reactive nitrogen (Cox and Roffey, 1977; Feick and Hainer, 1954):

$$\mathrm{PAN} \leftrightarrow CH_3COO_2 + NO_2 \quad \text{Equation (6)}$$

$$NH_4NO_{3\,(l)} \leftrightarrow NH_{3(g)} + HNO_{3(g)} \qquad \text{Equation (7)}$$

Higher temperatures push both these equilibria towards the right, i.e. resulting in thermal decomposition of gaseous peroxyacetyl nitrate (PAN: $CH_3COO_2NO_2$) and ammonium nitrate (NH_4NO_3) aerosol particles, effectively reducingthe atmospheric lifetimes of these two species. The impacts of 21st century climate change on global atmospheric composition, via reaction (Eq. (6)), have been investigated by Doherty et al. (2013). For a temperature increase of +3K (typical for 2100 relative to present-day), the PAN lifetime in the troposphere approximately halves (from 4 to 2.5 hours at mean surface temperatures of 290 K; and from 6 to 3 months at mid- to upper-tropospheric temperatures of 250 K). As PAN is a major component of tropospheric NO_y, climate change may significantly reduce the size of the NO_y reservoir, reducing the long-range (or intercontinental) transport of NO_y (Doherty et al., 2013).

Liao et al. (2006) find that climate change effects (specifically the SRES A1B scenario from 2000 to 2050) leads to reduced concentrations of NH_4^+ aerosols over East Asia, and attribute this to temperature increases acting via Eq. (7). Similar results were found over the US (Pye et al., 2009).

Changes in the stratospheric source of HNO_3 are also likely as a consequence of a changing climate. Much like the predicted increase in tropospheric O_3 from enhanced stratosphere-troposphere exchange (STE), driven by a more intense Brewer-Dobson Circulation, the stratospheric O_3 enters the troposphere with some NO_y as HNO_3. This is a small source currently estimated to be ~1 Tg N yr^{-1}, but STE is projected to increase by 50-100% over the 21st century, so this NO_y source may ~double. Stratospheric NO_y and O_3 may show different trends, so it may be more complicated than just knowing the STE air mass flux (most models just add NO_y with a fixed ratio to O_3).

5.1 Lightning-climate interactions

Lightning NO is an important natural source of tropospheric NO_x, especially the tropical upper troposphere (Schumann and Huntrieser, 2007). Nitric oxide (NO) is formed following the dissociation of molecular oxygen and N by the lightning discharge in air. Atmospheric composition is modified as described in the companion paper by Monks et al. (2014).

The effects of climate change on lightning and NO_x production have been investigated by Toumi et al (1996), and by Reeve and Toumi, (1999) suggesting increases in both lightning and NO_x production. The estimates of increased NO_x production in a warmer climate are rather variable and range from 4 to 60% per degree K (surface temperature change), Schumann and Huntrieser, 2007; and Williams, 2005). More recent analyses by Romps et al. (2014) based on the Convective Available Potential Energy (CAPE) and precipitation rate indicate values of 12± 5% $^{o}K^{-1}$.

Taking a value towards the lower end of the range of reported temperature responses, of 10% K^{-1} and a temperature change of $4^{o}K$ by 2100, yields an increase in lightning NO_x production from 5 to 7 Tg N yr^{-1}.

6 ORGANIC NITROGEN

Gaseous organic nitrogen exists in the atmosphere in both oxidized (peroxy acetyl nitrate PAN, and related compounds) and reduced forms, including amines, amino acids and urea. Organic nitrogen also occurs in particulate matter and in rain and snow and from the methodology for chemical analysis it is not always clear in whether the organic nitrogen was in reduced or oxidized form. The oxidized gaseous forms and PAN especially, are important as a reservoir of ozone precursors for photochemical oxidant formation (Singh and Hanst, 1981), while interest in the gaseous reduced forms and ON in aerosols and precipitation is primarily through their contribution to nitrogen deposition (Jickells et al., 2013).

Organic nitrogen in the tmosphere has been reviewed recently by Cape et al. (2011), Cornell et al. (2011) and Jickells et al. (2013). These reviews cover available measurements, atmospheric cycling, and provide a technical discussion on analytical methods, their comparability and statistical caveats for data treatment. In this section a general description of atmospheric ON, its sources, relevant properties and relations to the N cycle and the likely effects of changes this century are described. Gaseous oxidized organic nitrogen compounds are treated separately, as the literature, and motivation are distinct.

6.1 Atmospheric relevance

Organic nitrogen is a ubiquitous component of the atmosphere, mainly found in aerosols and precipitation, although present also in the gas phase (Cape et al., 2011; Cornell et al., 2011; Jickells et al., 2013). Atmospheric concentration data for the aerosol fraction in literature often refer to the water-soluble fraction of ON (WSON), more frequently investigated as it is considered to be more bioavailable (Seitzinger and Sanders, 1999) and climate relevant. Aerosol WSON atmospheric concentrations range from a few to few tens of nmol N m^{-3} in a selection of remote sites by Jickells et al. (2013), reaching concentrations as high as ~150 nmol N m^{-3} in the Po Valley (Montero-Martinez et al., 2014) and up to 2 µmol N m^{-3} at Quingdao (China) (Shi et al., 2011). The above aerosol concentrations determine WSON in rainwater ranging between 5 µmol L^{-1}, in remote regions, and >100 µmol L^{-1} as measured in China (Cornell et al., 2011).

The water-soluble fraction of ON contribution to total N in aerosol and rainwater has been investigated in a number of studies, with results ranging from a few percent to more than 40% (Cornell et al., 2011). Jickells et al. (2013) reports a collection of rainwater WSON datasets from around the world from the studies of Cornell et al. (2003, 2011) and Zhang et al. (2012), resulting in an average ON contribution of 24%. Similar contributions, ranging from 19 to 26%, have been observed for aerosols in many other studies (Zhang et al., 2002; Chen et al., 2010; Lesworth et al., 2010; Kunwar and Kawamura, 2014; Miyazaki et al., 2014; Montero-Martinez et al., 2014). Nevertheless, lower WSON/TN contributions have been also reported: 6% in Delaware, USA (Russell et al., 2003), 13% in Crete (Violaki et al., 2010), 16% in the outflow from northeast India over the Bay of Bengal (Srinivas et al., 2011) and 10% in paired urban-rural sites in Georgia (Rastogi et al., 2011). Higher contributions seem, instead, typical of China

(Shi et al., 2011; Zhang et al., 2012), likely due to the use of organic manures and urea as fertilizers in agriculture (Jickells et al., 2013).

It is worth highlighting that in one of the few studies in which total ON (and not WSON) was measured, the ON/TN ratio was of the order of 70% (western North Pacific in summer) (Miyazaki et al., 2010), suggesting an important contribution from water-insoluble ON. Russell et al. (2003) also showed an important fraction of aerosol ON in water-insoluble form. Other investigators (Li and Yu, 2004; Duan et al., 2009) which measured the total ON have not confirmed such a result. Finally, the model approach of Kanakidou et al. (2012) estimated ON as 26% of TN deposition, globally.

These numbers provide an insight into the importance of atmospheric ON in the N cycle, even though a full understanding is far from being achieved. In particular, ON can be considered important in the long-range transport of N (e.g., Singh and Hanst, 1981; Gorzelska and Galloway, 1990; Neff et al., 2002; Matsumoto and Uematsu, 2005) because its removal processes tend to be less effective than those for nitrate and ammonium, which are generally deposited closer to their sources (Cornell et al., 2011).

At least a fraction of ON is known to be bioavailable (Timperley et al., 1985; Peierls and Paerl, 1997; Seitzinger and Sanders, 1999) therefore its deposition can provide nutrients for land and marine ecosystems. Nevertheless, the effects of ON on the surface ocean are unclear due to the large uncertainty in the sources and magnitudes of deposition. Even less is known about the potential human and ecosystem toxicity of ON (Paumen et al., 2009).

Recently, atmospheric ON has received attention because of its light-absorbing properties (Desyaterik et al., 2013). Reactions leading to the formation of ON compounds in aerosol particles or evaporating droplets have been indicated as potentially important for the formation of atmospheric brown carbon (Noziere et al., 2007, 2009; Shapiro et al., 2009; Nguyen et al., 2012; Powelson et al., 2014; Lee et al., 2013).

6.2 Chemical composition

Atmospheric ON is a sub-set of the organic carbon, and in analogy with the latter, is a complex mixture of compounds with different properties and origin (e.g., Saxena and Hildemann, 1996; Jacobson et al., 2000; Neff et al., 2002). Complementary to the total ON (or WSON) determination approach, many studies have focused on measuring the concentration of individual N compounds or groups of compounds in air, aerosols or rainwater. Given the difficulties of measuring total ON, this approach is the usual course in the gas phase.

Although this approach will never account for the whole ON, it can be useful in providing insights to sources and to clarify the contribution of single species to ON. Compounds analysed in individual studies include amines, amino acids, urea, nitrophenols, alkyl amides, N-heterocyclic alkaloids and organic nitrates (Cape et al., 2011; Jickells et al., 2013), none of which resulted dominating the ON composition. This suggests that a large fraction of ON is associated with high molecular weight polymers, constituting the humic-like materials (HULIS) (Chen et al., 2010).

This approach has shown that in certain environments and conditions, some compounds make up a consistent fraction of atmospheric ON. For instance, amino acids have been reported to account for up to 50% in Tasmania (Mace et al., 2003a), while Facchini et al. (2008) reports dimethyl- and diethyl-amines contributing 35% of aerosol ON over the Eastern North-Atlantic Ocean. On the contrary, in other studies these are only minor components (e.g., Mace et al., 2003b; Mace et al., 2003c; Müller et al., 2009; Violaki et al., 2010). Urea was also shown as an important contributor (>20%) by Cornell et al. (2001) and Mace et al. (2003a) in Hawaii and Tasmania, but was reported as a minor ON component in other sites (Mace et al., 2003b; Mace et al., 2003c). Recently, Zhang et al. (2012) showed that urea represents more than 40% of rainwater WSON in China where urea is widely used as a fertilizer.

Recently, ultrahigh resolution mass spectrometry has provided new insights into ON chemical composition in aerosol and rainwater. N-containing molecules have been reported, for instance, by Rincon et al., 2012; Cottrell et al. (2013); O'Brien et al. (2013); Zhao et al. (2013); and Kourtchev et al. (2014), accounting for 40 to more than 50% of the total identified molecules in their samples, for a total of thousands of compounds. These studies suggest that ON is made of both oxidised (organonitrates, nitroxy-organosulfates) and reduced (amines, imines, imidazoles) N species. Altieri et al. (2009; 2012) found similar results, with more than two-thirds of the detected ON compounds containing reduced nitrogen. Moreover, they observed significant chemical composition differences between marine and continental samples, concluding that, although the concentrations and percent contribution of WSON to total N is fairly consistent across diverse geographic regions, the chemical composition of WSON varies strongly as a function of source region and atmospheric environment. LeClair et al. (2012) reported that approximately 63% of the CHNO and 33% of CHNOS compounds observed in Fresno radiation fog samples exhibited a loss of HNO_3, suggesting that besides organonitrates, there might be other N containing functional groups present, such as amines, imines, and nitro groups.

These techniques detect ON compounds in a wide range of molecular weights with carbon number between 2 and 35 (Zhao et al., 2013; Cottrell et al., 2013). Nevertheless, Chen et al. (2010) has demonstrated that N containing molecules can have masses greater than 1 kDa.

6.3 Organic nitrogen sources

The complexity of ON chemical composition is reflected by its sources. ON source attribution was tentatively achieved in different studies based on size distribution, correlation with source tracers, multivariate analysis and isotopic ratios.

Many investigators report a significant spatial or temporal correlation between ON and inorganic N in aerosol and rainwater samples, with ON constituting roughly a quarter of total N in many environments (Cape et al., 2004; Zhang et al., 2012). Considering that inorganic N emissions are globally dominated by anthropogenic sources, ON has likely an important anthropogenic component (Zhang et al., 2012; Jickells et al., 2013). Many papers highlight important anthropogenic ON sources (e.g., Cornell et al., 2001; Mace et al., 2003c; Chen et al., 2010; Iinuma et al., 2010; Rastogi et al., 2011; Zamora et al., 2011; Zhang et al., 2012;

Kourtchev et al., 2014; Violaki et al., 2010; Cape et al., 2004; Bencs et al., 2009). More in detail, ON seems to present higher correlation with NH_4^+ than NO_3^- (Zhang et al., 2012, Cape et al., 2004; Srinivas et al., 2011). This points to an atmospheric processing of ON similar to that of reduced nitrogen, or to similar sources (Jickells et al., 2013). Indeed, several papers evidence ON formation processes via interactions between organic matter and reduced N (ammonia, amine compounds or HNCO and related gases) like Nguyen et al. (2012), Lee et al. (2013) and O'Brien et al. (2013). Nevertheless, also ON formation through NO_x or NO_3 radical chemistry is reported in the literature (e.g., Zhao et al., 2013; Fry et al., 2013).

Notwithstanding the very likely global dominance of anthropogenic sources, natural sources of ON have been reported both in the marine (Spokes et al., 2000; Cornell et al., 2011; Mace et al., 2003a; Facchini et al., 2008; Müller et al., 2009; Miyazaki et al. 2010; Kunwar et al., 2014) and continental (Miyazaki et al., 2014; Kieloaho et al., 2014; Laitinen et al., 2014) environments.

As for formation processes, primary ON sources have been reported associated with soil suspension (Chen et al., 2010), sea spray (Miyazaki et al., 2010; Barbaro et al., 2011; Scalabrin et al., 2012) and biomass burning (Desyaterik et al., 2013; Zamora et al., 2011; Mace et al., 2003b; Srinivas et al., 2011; Violaki et al., 2011).Evidence of the importance of secondary ON formation has been presented for a range of environments, involving a number of precursors (De Haan et al., 2011; Nguyen et al., 2012; Rincon et al., 2012; Fry et al., 2013; Lee et al., 2013; Miyazaki et al., 2014; O'Brien et al., 2013; Zhao et al., 2013; Kourtchev et al., 2014). Furthermore, Organic N, amines in particular, is known to play a role in atmospheric new particle formation (Murphy et al., 2007; Kurten et al., 2008; Smith et al., 2010; Kirkby et al., 2011).

Concluding, Jickells et al. (2013) summarises atmospheric ON sources in: 1) Soil dust, including in this source both ON associated with soil organic matter itself and the adsorption of ON onto dust particles; 2) Biomass burning; 3) Marine emission both direct and via emissions of gaseous precursors; 4) Anthropogenic and agricultural sources.

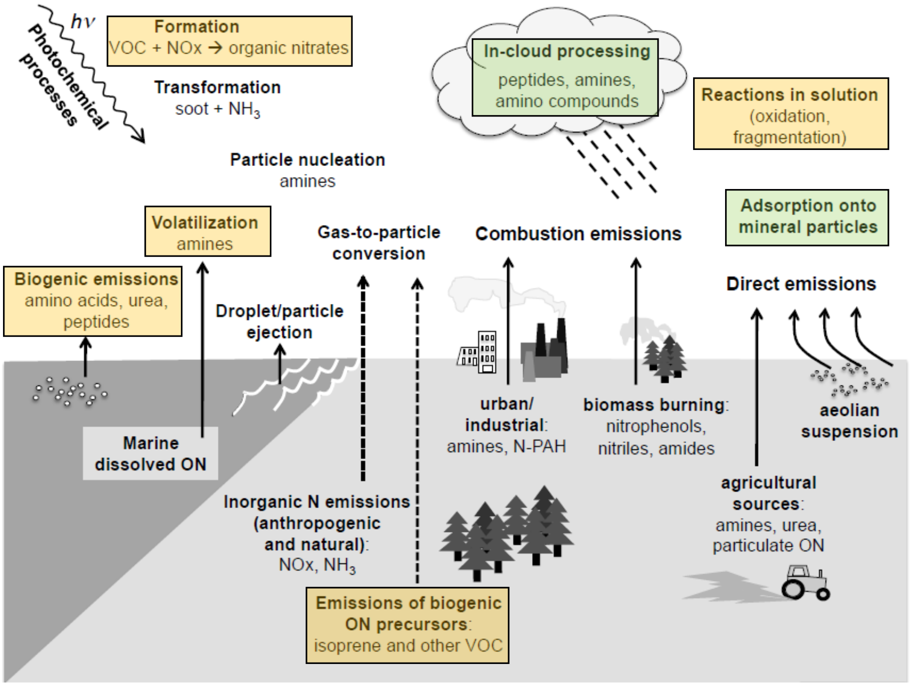

Figure 8: Processes where increased temperatures would be expected to increase atmospheric ON (orange) or decrease ON (green); no colour code implies uncertain effects. Adapted from Jickells et al. (2013).

6.4 Effects of future climate change on ON

Although predicting the effects of future changes in climate on ON is uncertain, given the current state of knowledge of the relative contributions of the different sources of ON in the atmosphere, some general points can be made:

1. Observed spatial and temporal patterns of ON concentrations and deposition correlate positively with those of NO_y and NH_x, it seems likely therefore that the projected increases in inorganic N_r will be associated with increases in ON;
2. For material derived from resuspension of soils, periods of prolonged drought and/or increased wind speeds would lead to greater amounts of airborne material than at present;
3. For material derived from biomass burning, future patterns of biomass burning (whether natural, from increased drought, or man-made, from changes in land use) will affect ON emissions;
4. Increases in average temperatures would be expected to lead to increased atmospheric concentrations of volatile and semi-volatile organic compounds, including ON species, and in particular amines and urea, both of which are

related to agricultural practices. Increased emissions of volatile organic compounds (VOCs) would provide greater substrate concentrations for reactions which form atmospheric ON. Increased sea-surface temperatures would also lead to increased volatilisation of ON from the sea surface layer.

5. Increases in the oxidised nitrogen (NO_y) content of the atmosphere would lead to faster reaction and conversion of organic matter into N-containing material, probably in the aerosol phase, leading in turn to increased aerosol concentrations of ON. Similarly, increased oxidising capacity would lead to faster conversion of hydrocarbons into oxidised organic matter which would be expected to act as a substrate for subsequent reaction with both reduced and oxidised forms of N.
6. Changes in agricultural practice, could lead to large changes in ON emissions, e.g. changes in the use of urea as a fertilizer, or changes in the management of animal wastes.

The evidence, while largely qualitative suggests increases in the absolute quantity of ON in the atmosphere due to changes in climate and the amount of N_r fixed by natural and anthropogenic activity. The ON processes which are sensitive to changes in climate and land use are summarised in Fig. 8. However, the knowledge of atmospheric processing and lifetimes of the chemical components preclude quantitative estimates of the changes this century.

6.5 Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN).

Acyl peroxynitrates (APNs) are produced in the boundary layer and lower free troposhere during the photochemical oxidation of volatile organic compounds (VOC) in the presence of NO_x (Cox and Roffey, 1977). The mixing ratios of these compounds are dominated by PAN with measured values commonly in the range 0.1 to 3 ppbV in Europe and North America (McFadyn and Cape, 1999, Parrish et al., 2004), with PAN contributing 80-90% of the speciated APN mesurements (Roberts, 1990). In a study of mixing rations and fluxes of speciated APNs over a Ponderosa pine forest, PAN values were in the range 200 to 500 pptv while PPN and MPAN values were generally 20 to 50 pptv (Wolfe et al., 2009). A particular interest in APNs has been their role as an atmospheric reservoir of $NO_{y.}$ APNs are subject to thermal decomposition, being stable in the cool upper troposphere and yet may decompose at lower altitudes and higher temperatures (Parrish et al., 2004). Through these processes APNs can transport NO_y over substantial distances and contribute to ozone formation remote from the NO_x sources.

The temperature sensitivity of PAN through thermal decomposition makes these compounds sensitive to changes in climate as noted in section 5, but important effects also appear at the atmosphere-surface interface over terrestrial ecosystems. Direct measurements of PAN deposition to a grassland were made by Doskey et al., (2004), who showed that thermal decomposition was a greater removal mechanism within the boundary layer than dry deposition to the grassland. Wolfe et al., (2009) reported flux measurements of APNs, above a Ponderosa pine canopy in California, showing daytime deposition fluxes of peroxyacetyl nitrate and deposition velocities peaking at ~5mm s^{-1}) at mid day and very small deposition velocities at night (~1 mm s^{-1}). Daytime deposition velocities of PPN were larger peaking at 13 mm s^{-1}, and were similar to those of PAN at night, while deposition velocities of MPAN were similar to those of PAN. In the case of PPN and MPAN the fluxes were an order of magnitude smaller than those of PAN, thus the overall flux was dominated by PAN. The dominant site of uptake within plant canopies for PAN appears to be stomata, from both laboratory and field study. However, night-time deposition values suggest that cuticular uptake contributes to the total deposition flux, and on average may be responsible for between 20 and 30% of the total deposition.

Measurements over Ponderosa pine by Farmer and Cohen (2008), suggest that in canopy chemical production of OH substantially modifies the fluxes of NO_y and VOC species, within and above the canopy. Further it is clear from their work that the exchange of O_3, NO_x and BVOC is regulated by solar radiation and depends exponentially on temperature, but predictions of the net effect of expected changes in climate have not been quantified. The effects of climate on PAN, PPN and MPAN may change the fate and lifetimes of these species in plant canopies, but since their contribution to nitrogen budgets at regional scales is small, the impact on the wider global nitrogen cycle is limited.

7 EFFECTS OF GLOBAL CHANGE ON ECOSYSTEM/ATMOSPHERE EXCHANGE OF REACTIVE NITROGEN

A wide range of atmospheric N_r compounds (reduced N_r including gaseous NH_3, amines and aerosol NH_4^+; and oxidised N_r including gaseous NO, NO_2, HONO, HNO_3, PAN, PPN and aerosol NO_3^-) are emitted by, and/or dry-deposited to, the Earth's surface (vegetation, soils, water bodies, built-up areas) (Flechard et al., 2011). The sign and magnitude of their exchange fluxes are governed not only by their chemical properties, but also by meteorological, physical, chemical and biological processes. For many of these species (e.g. NH_3, HONO, NO_2) the exchange can be bi-directional (Flechard et al., 2013; Oswald et al., 2013; Neirynck et al., 2007), with emissions occurring when the surface potential exceeds the atmospheric concentration, or vice-versa. Soils have recently been shown to be a source of HONO to the atmosphere (Su et al 2011).

All transfer processes between the atmosphere and the surface (vertical turbulent transport, ecosystem air column chemistry, surface/vegetation sink or source strength) are potentially affected by global change, not just through altered climate and elevated CO_2 and the knock-on effects on global vegetation and the ocean, but also (i) through changes in the mixing ratios of other pollutants such as O_3 and SO_2 that affect stomatal function and/or surface chemical sinks, (ii) through changes in land use, land cover and agricultural as well as silvicultural practices, and even (iii) through the feed-back of elevated N_r deposition on ecosystem functioning.

7.1 Impacts on processes regulating surface N_r sink/source strength

7.1.1 Vertical atmospheric transport

Compounds whose deposition rates are particularly sensitive to atmospheric turbulence include those for which vegetation is a perfect sink, including nitric acid, and those contained in aerosols. Thus, surface wind speed, friction velocity, atmospheric stability and surface roughness control the rates of vertical turbulent transport of N_r trace gases and aerosols through the surface layer and within the canopy. The aerodynamic (R_a) and viscous sub-layer (R_b) resistances to dry deposition are both inversely proportional to the friction velocity (Monteith and Unsworth, 2013). A comparison over the period 1988–2010 of recent linear trends in global surface wind speeds from satellite data, from in situ data and from atmospheric reanalyses, showed (i) a pattern of positive and negative trend bands across the North Atlantic Ocean and positive trends along the west coast of North America, and (ii) a strengthening of the Southern Ocean winds, consistent with the increasing trend in the Southern Annular Mode and with observed changes in wind stress fields (Fig. 2.38 in IPCC, 2013). The decadal trends in surface winds on land were mostly of the order of 0 to +0.2 m s^{-1} $decade^{-1}$, with large areas of the Southern Pacific experiencing increases of up to +0.5 m s^{-1} $decade^{-1}$. Future trends in wind speed are unclear, but it is clear that increases of such magnitudes enhance atmospheric dry removal rates and shorten pollutant atmospheric lifetimes.

Similarly, changes in land cover and associated surface roughness are likely to affect the atmospheric lifetime of gases and aerosol compounds alike. Large-scale deforestation, for example, would reduce the deposition rate of aerosol significantly, while changes in crop types and tree species would have more subtle, but potentially important effects. For example, Davidson et al. (1982) showed that aerosol deposition rates to different grass species could differ by a factor of 10, in response to the microstructures (e.g. hairs) of the leaves.

7.1.2 Stomatal exchange

The flux of gaseous N_r pollutants into or out of sub-stomatal cavities of vascular plants is controlled primarily by the stoma-atmosphere concentration gradient and by stomatal conductance (G_s) (Baldocchi et al., 1987). Free-air carbon dioxide enrichment (FACE) experiments have suggested that elevated CO_2 concentrations result in a substantial reduction in ecosystem-scale G_s (typically -20% to -30%) (Ainsworth and Rogers, 2007), while the projected elevations in tropospheric O_3 will also reduce G_s by typically 10% to 20% (Wittig et al., 2007). The combined impacts on G_s of elevated CO_2 and O_3 in a future climate are less clear, however, due to nonlinear interactions between plant responses to CO_2 and O_3. For example, the CO_2-induced reduction in G_s helps alleviate future O_3 plant damage by mitigating stomatal phytotoxic O_3 uptake (Sitch et al., 2007).

Rising temperatures will on the other hand also impact G_s through a further reduction in stomatal opening under heat waves, or conversely through an increase in G_s in colder climates and an extension of the growing season. Changes in precipitation patterns will however likely affect G_s to a larger extent than temperature if they result in more frequent droughts during the growing season. The N_r species whose dry deposition is most affected by changes in G_s is probably NO_2, due to its low affinity for non-stomatal sinks (Flechard et al., 2011), but the effect could also be significant for water insoluble organic N compounds such as peroxyacyl nitrates (PANs).

In the specific case of NH_3, unlike other N_r species, another major control of the stomatal flux is the stomatal compensation point (Meyer, 1973), i.e. the leaf-level NH_3 concentration that reflects the thermodynamic equilibrium with apoplastic NH_4^+, which itself results from cellular exchange and the balance of cytoplasmic consumption and production (Farquhar et al., 1980; Massad et al., 2010b). The combined temperature-dependent solubility (Henry's law) and dissociation constants result in an effective Q_{10} of 3-4 (Sutton et al., 2013b), which would see the NH_3 compensation point approximately double with a temperature increase of 5 K. This is the same effect that will increase emissions from agricultural point sources in a future climate (cf Sect. 4.1.1). For vegetation this effect only holds, however, if the emission potential represented by the apoplastic Γ ratio ($\Gamma = [NH_4^+]/[H^+]$) remains constant. Ecosystem modelling (e.g. Riedo et al., 2002) suggests that variations in apoplastic $[NH_4^+]$ might be expected in response to global change, e.g. with rising temperature and CO_2 affecting primary productivity and soil/plant N cycling. Apoplastic pH itself could also be affected by global change; a doubling of CO_2 (from 350 to 700 ppm) can alkalinise the apoplast by 0.2 pH units (Felle and Hanstein, 2002); similarly, droughts can induce increased apoplastic alkalinity by a few tenths of a pH unit (Sharp and Davies, 2009; Wilkinson and Davies, 2008). Because nitric oxide (NO) is an important internal signaling compound that is also released in response to ozone exposure (Velikova et al., 2005; Ederli et al., 2006), increased ozone exposure in a future chemical climate might lead to elevated compensation points for NO. This NO source is currently not usually represented in exchange models.

7.1.3 Non-stomatal plant surfaces

Vegetation surfaces other than stomatal apertures (leaf cuticule, stems, bark of tree trunk and branches, also senescent leaves) are generally considered efficient sinks for NH_3 and especially HNO_3, particularly so if these surfaces are wet from rain or dew. Soluble N_r gases will readily be taken up by surface water films, although their affinity for NH_3 is expected to decrease as pH increases beyond seven (Walker et al., 2013), or if the NH_x accumulated in surface wetness leads to a saturation effect, reducing the sink strength (Jones et al., 2007). The atmospheric SO_2 to NH_3 molar ratio, or the total acids ($2*SO_2 + HNO_3 + HCl$) to NH_3 ratio, have been used in some inferential or chemical transport models (CTM) to scale non-stomatal resistance to surface NH_3 deposition (Massad et al., 2010a; Simpson et al., 2012).

Chemical composition and size of the wetness pool are thus key to the N_r gas removal efficiency (Flechard et al., 1999). It follows that global changes affecting the frequency and intensity of rain or dew, the subsequent evaporation rate of surface water, and the relative abundances of atmospheric alkaline compounds (NH_x, amines from agriculture; base cations from sea spray and soil erosion) versus acidic species (NO_y, SO_x, HCl from traffic, household and industrial sources) are likely to affect non-stomatal sink strengths for most water-soluble N_r species. Rising atmospheric CO_2 itself will acidify rainfall and any plant or terrestrial surface wetness, as well as freshwater and the ocean. As an illustration, the pH of pure water in equilibrium with ambient CO_2 at 15°C is 5.60 for current (399.5 ppm) CO_2 concentrations; this would drop to 5.59, 5.53, 5.48 and 5.41 for the 2100 CO_2 levels, predicted in the Representative Concentration Pathway scenarios, of 420.9 ppm (RCP2.6), 538.4 ppm (RCP4.5), 669.7 ppm (RCP6.0) and 935.9 (RCP8.5), respectively (IPCC, 2013). In real solutions, buffering effects could mitigate the impact of CO_2, but global ocean surface pH projections for 2100 do range from 8.05 (RCP2.6) to 7.75 (RCP8.5), versus 8.1 currently, which will mitigate the temperature-induced increase in sea NH_3 emissions.

Global atmospheric emission projections for NO_x and NH_3 for the year 2100 mostly range from around 15 to 75 Tg N yr^{-1} and from around 45 to 65 Tg N yr^{-1}, respectively, compared with similar current emissions levels of around 40 Tg N yr^{-1} for both; those for SO_2 emissions mostly range from around 15 to 40 Tg S yr^{-1} in 2100, versus around 55 Tg S yr^{-1} currently (van Vuuren et al., 2011a, 2011b). If one defines the global emission ratio ($2*SO_2 + NO_x$) / NH_3 (on a molar basis) as a proxy for global atmospheric acidity/alkalinity, this yields a current global value of around 2.2 mol mol^{-1}, while values based on 2100 emission projections range from 0.4 to 2.4 mol mol^{-1}, with a mean value of 1.2 mol mol^{-1}, i.e. a decrease of the ratio of 45%. If, as suggested by Sutton et al. (2013b), a global temperature rise of 5 K induces an additional – and generally unaccounted for - increase of 42% in global NH_3 emissions (on top of those attributed to increased anthropogenic activities), the reduction in the ratio is 61%. For Europe, where emission reductions are likely to continue for SO_2 and NO_x, by 75-90% and by 65-70%, respectively, by the year 2050, and with more or less constant NH_3 emissions (Engardt and Langner, 2013; Simpson et al., 2014), the ratio would drop by 75% from around 2.3 to 0.6 mol mol^{-1}. The resulting drop in acidity of water films on terrestrial plant surfaces (also reflected in projected reductions in acid deposition – see e.g. Lamarque et al., 2013) is expected to reduce non-stomatal NH_3 uptake significantly, and is a direct consequence of mitigation policies likely being implemented throughout the world for SO_x and NO_x emissions, but not for NH_3 except in very few countries.

This first-order estimate in the acidity ratio ignores nonlinearities caused by a change in the lifetime of individual atmospheric pollutants in response to climate and composition change. Rising temperatures would enhance chemical reaction rates on leaf surfaces as well as in the atmosphere (e.g. SO_2 oxidation to SO_4^{2-}), also affecting pH, but perhaps more significantly, a warming would favour the partitioning of dissolved species in water films (NH_3, SO_2) - and of volatile N_r-containing aerosols (e.g. NH_4NO_3, NH_4Cl) - towards the gas phase. The non-stomatal surface resistance to NH_3 deposition has been shown over grassland to be both relative humidity- and temperature- dependent, roughly doubling with every additional 5 K (Flechard et al., 2010), consistent with solubility and dissociation themodynamics of NH_3(gas)/$NH_3.H_2O$/NH_4^+.

Surface warming is thus generally expected to reduce the non-stomatal N_r sink strength, especially for NH_3, with the notable exception of frozen surfaces, over which the effect of warming could be opposite. Surface/atmosphere NH_3 flux measurements over moorland have in fact shown that at sub-zero temperatures the non-stomatal sink is much reduced, but also that the canopy resistance decreases as surface ice or snow melts (Flechard and Fowler, 1998). Warming is expected to be strongest in the mid and especially higher latitudes (IPCC, 2013), such that vast regions in temperate to boreal climates could experience much shorter winters and significantly reduced numbers of frost days, increasing the wintertime N_r sink strength. Further, because ambient NH_3 concentrations should increase globally (higher ground-based emissions, and a decreased volatile aerosol NH_4^+/total NH_x fraction), predicting the net impact on deposition fluxes is a challenge. Similarly, a reduced aerosol NO_3^-/total NO_y fraction, and relatively higher HNO_3 concentration, ought to favour overall greater NO_y dry deposition, since HNO_3 deposits much faster than NH_4NO_3 aerosol (Nemitz et al., 2009; Fowler et al., 2009).

7.1.4 Soil surface exchange

Soils and surface leaf litter are both sinks and sources of N_r. The expected impacts of global change on the soil-level source strength for NH_3, NO and N_2O are described in detail elsewhere in this review (Sect. 4.1.1), and, in the case of NO have been reviewed by Pilegaard (2013) and by Ludwig et al. (2001), For agricultural soils the changes are essentially controlled by agricultural management and cropping practices (especially fertilizer inputs: form, quantity, technique and timing of application), and by changes in climate that affect soil temperature and moisture, impacting on the turnover of soil organic matter (heterotrophic respiration), fertilizer infiltration, NH_3 volatilisation and the rates of nitrification and denitrification (Butterbach-Bahl and Dannenmann, 2011; Sutton et al., 2013b; Flechard et al., 2013). On the other hand, the N_r sink strength of soils and litter surfaces is governed by the same processes – and should be similarly impacted by changes in meteorological, physical and chemical drivers – as the canopy non-stomatal sink (see above). One essential difference, though, is that soil and decaying plant material in the litter layer are much more buffered media than is leaf surface wetness, such that smaller shifts in pH may be expected in response to the same atmospheric drivers. However, soil acidification may result from increased agricultural intensification in the 21st century, from increased N deposition onto semi-natural systems, and possibly from global hydrological changes impacting on soil oxygen availability and denitrification.

7.1.5 Chemical interactions during the exchange process

Global change may also impact air column chemical processing within and just above vegetation canopies, creating vertical flux divergence and altering the N_r sink (or source) strength. Here, for N, the main chemical interactions are those between NO, O_3 and NO_2 as well as the gas / aerosol partitioning involving volatile ammonium salts, primarily NH_4NO_3 and to a much lesser extent NH_4Cl.

Increasing global tropospheric O_3 concentrations (Sitch et al., 2007) should raise the within-canopy oxidation capacity for soil-emitted NO, thereby transforming more soil NO into NO_2 which can be at least partially recaptured by the overlying canopy, thus reducing total NO_x emission (or increasing net NO_x deposition) (Duyzer et al., 2004). Near and in-canopy chemistry are driven by the sharp gradients in concentrations and meteorological drivers near the ground. Thus they represent subgrid process for typical chemical transport models, where the bottom layer in which chemistry is calculated typically averages over tens of meters. Most models apply empirical formulations of the in-canopy chemical conversion and subsequent canopy reduction of the NO emission (Yienger and Levy, 1995) that do not mechanistically respond to changes in vegetation and chemical climate. Applying a subgrid model within a chemistry-climate model to analyse the impacts of land cover and land use changes on atmospheric chemistry at the global scale by 2050, Ganzeveld et al. (2010) calculated that changes in atmosphere-biosphere fluxes of NO_x would be small, pointing to compensating effects: although global soil NO emissions were expected to increase by ∼1.2 Tg N yr^{-1} (+9%), decreases in soil NO emissions in deforested regions in Africa and elsewhere would be offset by a larger canopy release of NO_x caused by reduced foliage NO_2 uptake. More studies of this type are needed provide a more robust basis for prediction.

Recent advances in instrumentation to measure surface/atmosphere exchange fluxes of individual aerosol chemical components with micrometeorological techniques have led to the revelation that while effective deposition rates of sulfate are of the magnitude predicted by mechanistic aerosol deposition models (<2 mm s^{-1} for short vegetation and 1 to 10 mm s^{-1} to forest), measured deposition rates of NO_3^- often reach daytime values in excess of 50 mm s^{-1} (Thomas, 2007; Wolff et al., 2007; Ryder, 2010; Wolff et al., 2011). This observation is due to the fact that some of the aerosol NH_4NO_3 that passes the measurement height dissociates into NH_3 and HNO_3 before interacting with the surface and therefore deposits at an apparent deposition rate that reflects gas-phase deposition rather than physical interaction of particles with vegetation. The volatilisation of NH_4NO_3 is driven by the depletion of NH_3 and HNO_3 near and in canopies, due to their dry deposition, coupled with an increase in temperature which typically peaks at the top of the canopy during daytime.

The impact of near-surface column chemistry on the exchange flux actually depends (i) on the gradients in drivers of disequilibrium (relative mixing ratios of N_r species; gradients in temperature and relative humidity) and (ii) on the comparative time-scales of chemical reactions and turbulent transfer to/from the surface (Nemitz et al., 2000). Global warming will shift the NH_4-HNO_3-NH_4NO_3 equilibrium further towards the gas phase, which will reduce the concentrations of NH_4NO_3. However, as discussed above and in Sect. 4.1.1, NH_3 emissions are likely to increase. NO_x emissions might well decrease, but the oxidation capacity of the atmosphere that governs the conversion of NO_x to HNO_3 is more likely to increase and the change in absolute NH_4NO_3 concentrations is therefore difficult to predict accurately.

The contribution of NH_4NO_3 to European total aerosol concentration is demonstrated in Fig. 9 which summarises campaign-based measurements of submicron aerosol composition across a coordinated network. During the colder seasons in particular, NH_4NO_3 was the single largest contributor to PM_1 in north-west Europe, often exceeding the importance of organic aerosol and sulfates. Exceptions were sites on Crete (higher temperature), in Finland (few local emissions) and at high elevations sites (long transport time, no local emissions). Even at fairly remote sites such as the Scottish EMEP Supersite ‘Auchencorth Moss’, NH_4NO_3 often accounts for the bulk of the PM_{10} aerosol mass during pollution events (Fig. 10). Thus, the effect of climate change on the evolution of NH_4NO_3 has important consequences for exceedances of PM air quality objectives and for the climate system.

The impact of climate change on the interaction between aerosol volatility and surface exchange is less closely linked to changes in absolute temperature and humidity (these govern the overall atmospheric burden), but to changes in near-surface gradients in temperature, humidity and gas-phase concentrations. Increased solar radiation and reduction in evapotranspiration as a result of decreased stomatal conductance (see above) is likely to increase sensible heat fluxes and associated temperature gradients.

For the $NH_3/HNO_3/NH_4NO_3$ and $NH_3/HCl/NH_4Cl$ gas-aerosol equilibria, a surface warming and a lowering of relative humidity in a future climate would favor the faster depositing gas phase (NH_3, HNO_3) over the slower depositing NH_4^+ and NO_3^- aerosol. In addition, reduced NO_x emissions by 2100 (van Vuuren et al., 2011a) may result in lower HNO_3 concentrations and thus reduce the secondary inorganic aerosol sink for NH_3. The impact of these processes on the atmospheric lifetimes and travel distances for NH_3 and N_r in general, however, must be set against the expected (temperature-induced) increase in both non-stomatal resistance and in stomatal compensation point for NH_3, which would have opposite effects.

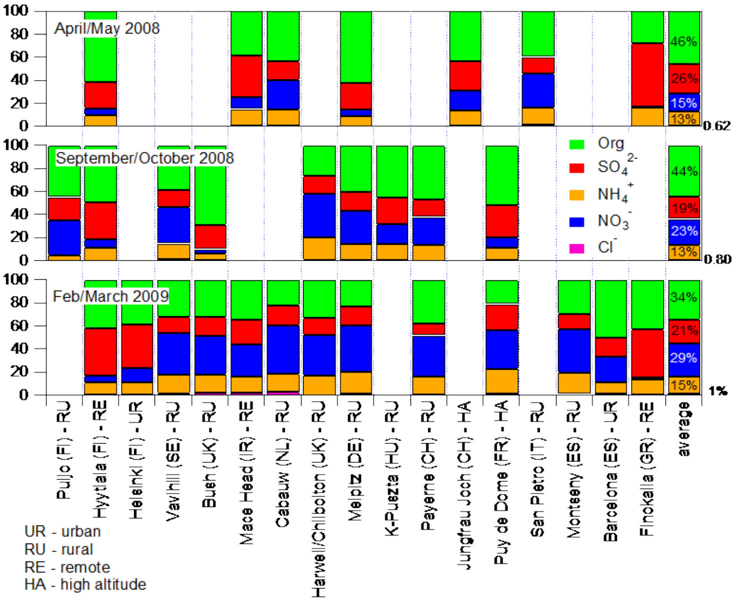

Figure 9: Relative (non-refractory) submicron aerosol composition measured with an Aerosol Mass Spectrometer (AMS) network during three pan-European EMEP / EUCAARI campaigns. The sites are arranged from North to South.

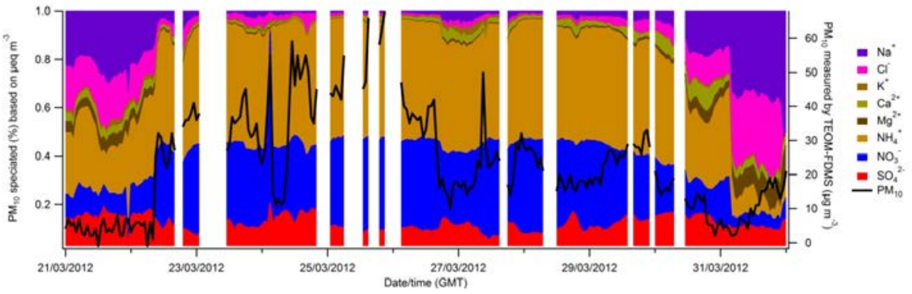

Figure 10: Relative PM_{10} water soluble aerosol composition during an example pollution event observed at a rural Scottish EMEP site (Auchencorth Moss).

7.2 Regional and global projections for nitrogen deposition

Future trends in total (wet and dry) atmospheric N_r deposition have been simulated on the basis of CTM runs forced by climate and emission scenarios (Lamarque et al., 2005, 2013; Engardt and Langner, 2013; Simpson et al., 2014). At the regional scale, European climate/chemistry/deposition studies suggest that with current emission projections the main driver of future N_r deposition changes is the specified future emission change (Engardt and Langner, 2013; Simpson et al., 2014). These two studies both found significant reductions in oxidised N concentrations and deposition over Europe, and much smaller changes (both increases and decreases) in reduced N deposition, with climatic changes in having only moderate impact on total deposition. These two studies also demonstrated that the lack of sulfur and oxidised N in the future atmosphere would result in a much larger fraction of NH_x being present in the form of gaseous NH_3. Simpson et al. (2014) predicted a large increase in gaseous NH_3 deposition in most of Europe, but with large corresponding decreases in aerosol NH_4^+. Although not the focus of their study, the change of NH_4^+ to NH_3, while not greatly reducing the European export, would result in shorter transport distances within Europe with likely important impacts on the protection of sensitive ecosystems.

A separate recent sensitivity study has revealed that the effect of NH_4NO_3 volatilisation near and in plant canopies lowers European surface concentrations of fine NO_3^- by typically 30% at the annual average (Nemitz et al., 2014). At the same time it increases the effective NO_3^- deposition by a factor of four. While some models are now able to account for some of this effect (e.g. the EMEP model; Simpson et al., 2012), it is not included in the majority of models. However, this effect has not yet been projected into the future to quantify the impacts of changes in climate.

Hemispheric N_r deposition projections (Hedegaard et al., 2013) also show that the impact of emission changes dominates and is in some areas (e.g. over Europe) up to an order of magnitude higher than the signal from climate change. Nonetheless, trends in total nitrogen (NH_x + NO_y) deposition in parts of the Arctic and at low latitudes *are* dominated by climatic impacts. At the global scale, Lamarque et al. (2013) simulated large regional increases in N_r deposition in Latin America, Africa and parts of Asia (under some of the scenarios considered) by 2100. Increases in South Asia were predicted to be especially large, and were seen in all scenarios, with 2100 values more than double those of 2000 in some scenarios. Region-averaged values under scenarios RCP2.6 and RCP8.5 were typically ~30–50% larger in 2100 than the current values in any region globally.

Most of these studies to date do not account for the full range of global change impacts on surface exchange processes. Surface exchange in most chemistry transport models (CTMs) is generally much simplified in dry deposition (downward-only) modules (Flechard et al., 2011) that cannot respond mechanistically to changes in the physical, chemical and biological drivers of stomatal, non-stomatal and soil sources or sinks. For example, multiplicative algorithms widely used to simulate G_s (Jarvis, 1976) are still the norm in these models, while photosynthesis-based approaches (e.g. Anav et al., 2012) would be needed to quantify the future impacts of rising CO_2 and O_3 on G_s and stomatal pollutant uptake (or release). Similarly, surface chemical interactions and their impact on non-stomatal sinks are not accounted for in CTMs. Indeed, Simpson et al. (2014) noted that modelling for especially NH_x components is limited by many factors, including process-uncertainties (Massad et al., 2010a; Flechard et al., 2013), problems of sub-grid heterogeneity (e.g. Loubet et al., 2001, 2009), bi-directional exchange (Wichink-Kruit et al., 2012, Bash et al., 2013), and lack of necessary and accurate input data. As one example, it may be argued that such models do not account for a likely increase in the overall (stomatal and non-stomatal) surface resistance to NH_3 deposition, some of which may be attributed to feed-backs: higher NH_3 exposure leads to more alkaline surfaces and higher plant N uptake and a higher NH_3 compensation point, with deposition a self-limiting process. Improved models which incorporate both better process descriptions and better input-data, are clearly needed to improve confidence inpredictions of future N-deposition.

Two further examples of impacts of climate change can be given, both through new sources (or forcing) of emissions: the possibility of new shipping routes in the Arctic regions, and temperature-induced changes in ammonia emission factors. With regard to shipping, the rapid retreat of the Arctic sea has been one of the most dramatic features of recent decades (Comiso, 2012; Corbett et al., 2010). According to Corbett et al. (2010), NO_x emissions from Arctic shipping in high growth scenarios will increase by a factor of ~4 by 2050 compared to 2004, or almost a factor of ~14 if high global shipping routes are diverted into Arctic areas. The impacts of these changes on the phyto-toxic ozone dose, (POD) and N-deposition have been explored on the regional scale using the EMEP MSC-W model (Simpson et al., 2012) by Tuovinen et al., (2013). As illustrated in Fig. 11, the impact of shipping emissions is concentrated along the Norwegian coast. Although the changes are not large, e.g. 50 mg (N)/m^2, these values are comparable to base-case deposition amounts, and are likely to be important for the sensitive ecosystems in Arctic Europe. These aspects, and also the results found for POD, are discussed further in Tuovinen et al. (2013).

Simpson et al. (2014) made a first estimate of the impact of such NH_3 emission increases over Europe for year 2050 simulations. They explored the impact of both 20 and 30% increases in NH_3 and calculated the exceedance of critical-levels (CL) for N. Comparison of these runs against the CL data (Fig. 12) shows that even a 30% increase in NH_3 will not bring exceedances back to 2000s levels, but such climate-induced increases cause CL exceedances that are substantially larger than those of the standard 2050 emission scenario. Policy studies in Europe and elsewhere have been unaware of this hidden potential for increases in NH_3 emissions. As noted by Sutton et al. (2013b), the approaches used to calculate and report NH_3 emissions for both CTM modelling and policy assessments need complete revision to cope this new paradigm.

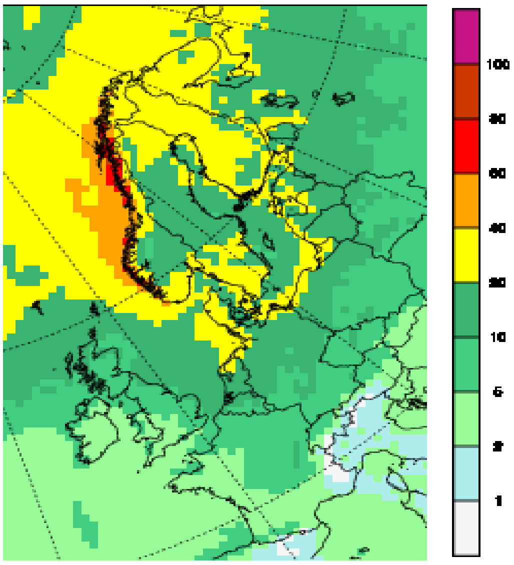

Figure 11: Increases in total Nr deposition (mg/m2) due to increased Arctic shipping emissions, including diversion routes in 2030. Results are relative to a 2030 base-case. Calculations from EMEP MSC-W model, redrawn from Tuovinen et al. (2013)

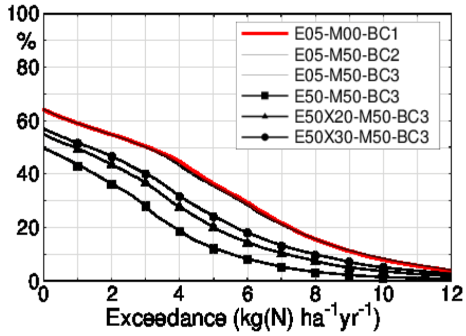

Figure 12: Frequency distribution of exceedances of the Critical Levels for eutrophying Nitrogen in Europe (EU28+). The red line (E05-M00-BC1) represents a year 2000 base-case and the E50-M50-BC3 scenario represents year 2050 with current emission estimates. The E50X20 and E50X30 scenarios illustrate calculations with 20% and 30% extra NH3 emission due to climate-induced evaporation. See Simpson et al., 2014 for more details.

8 THE EFFECTS OF CLIMATE AND LAND USE CHANGES ON THE WET REMOVAL OF NITROGEN COMPUNDS FROM THE ATMOSPHERE

The removal of N compounds from the atmosphere and their deposition to land surface by precipitation is known as ‘wet deposition’. Future climate change will cause changes in annual precipitation with some areas of the world being subject to increases in precipitation and others to decreases. Kjellstrom et al. (2011) used an ensemble of 16 regional climate models to show that in the 21st century the precipitation in northern Europe will increase and in the south of Europe, especially the Mediterranean area, it will decrease, with a zone in between where the change is uncertain. Changes in wet deposition of N will be driven mainly by changes in precipitation. However the degree of increase or decrease in wet deposition is expected to be smaller than changes to precipitation. The reason for this is that the supply of particulate matter in the atmosphere which can be wet deposited is itself controlled by precipitation. Historically, dryer years have been associated with higher levels of NH_4^+ and NO_3^- particulate concentrations in air. Therefore decreases in deposition due to reduced precipitation are expected to be partially offset by higher concentrations of NH_4^+ and NO_3^- in precipitation.

Certain atmospheric chemical transformations have reaction rates which depend on meteorology including temperature, humidity and the presence of cloud water. A particular example of this is the equilibrium reaction between ammonia gas and nitric acid vapour to form ammonium nitrate aerosol. The dissociation constant of ammonium nitrate is a strong function of temperature and varies by two orders of magnitude for typical ambient conditions (Seinfield and Pandis, 1998). Higher temperatures result in a shift towards the gas phase resulting in lower concentrations of ammonium nitrate, a pollutant which is associated with long range transport and contributes to N deposition through wet deposition. Changes in general circulation of air will also result in different patterns in the long range transport of N compounds and the areas in which N is wet deposited. Studies of the long range transport of particulate matter show that the natural inter-annual variation in circulation has a strong influence on N aerosol concentrations (Vieno et al., 2014). Kryza et al. (2012) found that inter-annual variation in annual precipitation could account for changes of 17% and wind direction variation for 14% in total annual N deposition for two European countries. Climate change may therefore lead to a re-balancing in the contributions to N deposition of long range transport and local sources as well as the relative contributions of dry and wet deposition.

An additional wet deposition mechanism by which N can be transferred to the surface is direct cloud droplet deposition. Most types of cloud form in the middle atmosphere and do not come into direct contact with the land surface. However, in mid-latitude regions the formation of orographic clouds in hill areas is a common occurrence due to the forced ascent and condensation of humid air. Such clouds are frequently short lived and the cloud droplets do not grow large enough to form into rain drops. However, where orographic cloud does come into contact with surface vegetation, the cloud water can be deposited to the surface by direct deposition driven by air turbulence (Fowler et al., 1990). The efficiency of this mechanism depends critically on vegetation type. In grassland areas cloud deposition is generally a much less efficient mechanism for N deposition than wet deposition by precipitation. However in regions of forested hills, cloud deposition can be the dominant process for the input of nitrogen to sensitive upland ecosystems (Błaś et al., 2008). The impact of future climate change is expected to result in a shift in climatic zones and could cause the migration of forests to higher altitude areas which were previously above the tree line. The consequence of this would be large increases in inputs of nitrogen due to the effect of cloud deposition.

9 EFFECTS OF CLIMATE AND LAND USE CHANGES ON C-N RESPONSES IN TERRESTRIAL ECOSYSTEMS

The close linkage between the terrestrial C and N cycles implies that perturbations of the C cycle, such as the anthropogenic increase in atmospheric CO_2 (and ensuing changes in plant production), man-made climate change (affecting the turnover rates of terrestrial C), or anthropogenic land-use change invariably have repercussions on the terrestrial N cycle (Zaehle, 2013). The level of understanding of these repercussions is generally low, owing to the lack of globally representative empirical studies and sufficiently tested global models (Zaehle and Dalmonech, 2011).

Observational evidence from ecosystem scale CO_2 manipulation experiments consistently shows that the magnitude and persistence of CO_2 fertilization strongly depend on the ability of the vegetation to increase its N acquisition (Finzi et al 2007; Palmroth et al 2006; Norby et al., 2010; Hungate et al., 2013). The sustained increase of vegetation production observed at some experimental sites was associated with increased root exudation and soil organic matter turnover, effectively redistributing N from soils to vegetation (Drake et al., 2011; Hofmockel et al., 2011). Other factors such as increases in N inputs from fixation generally played only a small role in forest ecosystems (Norby et al., 2010; Hofmockel et al., 2007). There is mixed evidence concerning the response of ecosystem N losses to elevated CO_2. The response of gaseous N losses (e.g. as N_2O) to elevated CO_2 depends on the response of ecosystem N turnover under elevated CO_2 and generally leads to an increase in N_2O emissions in ecosystems where N availability does not strongly limit plant growth (van Groenigen et al., 2011; Butterbach-Bahl and Dannenmenn, 2011).

In agreement with the experimental evidence, global modelling studies generally show a strong attenuating effect of the CO_2 fertilization on plant growth and land C storage due to reduced N_r availability (Sokolov et al., 2008; Thornton et al., 2009). Future projections of N cycle models that accounted for varying terrestrial N sources and losses (Xu-Ri and Prentice, 2008; Zaehle et al., 2010a) showed a wide range of responses of the terrestrial N cycle to increasing elevated CO_2 (Fig. 13). This is due to diverging representation of important N cycle processes, in particular those controlling in- and outflows of N from the ecosystem and the coupling of the C and N stoichiometry in plants and soils (Zaehle and Dalmonech, 2011; Zaehle et al., 2014). The increase in terrestrial N by up to 11 Pg N (+10%) during the period 1860-2100 in the LPX model was mostly determined by increasing biological N fixation under elevated CO_2 (Stocker et al., 2013). Over the same time period, the response of the O-CN model was determined by an increase of the vegetation and soil C:N ratios as well as increases in terrestrial N (3 Pg N; +2.5%) due to reduced N losses (Zaehle et al., 2010b). The projections by the CN-TEM model (Sokolov et al., 2008), which assumes that the total terrestrial N store is time-invariant, suggested an increase in terrestrial C between 1860 and 2100 by ~250 Pg C simply due to a prescribed increase in vegetation C:N and redistribution of N from soils to vegetation.

In response to increasing temperature, enhanced decomposition of soil organic matter consistently increases gross and net N mineralisation (Bai et al., 2013; Rustad et al., 2001). Increased mineralisation is generally, but not always, associated with increases in nitrification, and N_2O emissions. There is ambiguous evidence as to the response of N leaching losses, which in some cases increased and in others declined (Bai et al., 2013). Observed growth responses to warming are more diverse, partly owing to difficulties in measuring plant growth and its interannual variability (Rustad et al., 2001). In N-limited ecosystems, increased N mineralisation increases N uptake of vegetation, which causes a long-term fertilization effect in N limited forests (Melillo et al., 2002, 2011). In consequence, despite likely N losses due to warming, the higher C:N ratio in woody vegetation compared to C:N ratio of soil organic matter causes increased ecosystem carbon storage due to the redistribution of N from soil to vegetation (Melillo et al., 2011).

Global models include these mechanisms and consistently suggest an attenuation of the C loss under higher temperatures due to C-N cycle interactions. However, the available climate change projections vary widely in their global N cycle response, partly owing to differences in magnitude and regional patterns of temperature and precipitation changes (Stocker et al., 2013). In general, soil N stocks tend to decline in future projections, due to increased soil N mineralisation and increased ecosystem N losses (Fig. 12). These losses range between 5 and 10 Pg N (roughly 5-10%) between 1860 and 2100, depending on the model and scenario applied (Stocker et al 2013; Zaehle et al., 2010a). Although regionally there are increases in vegetation N associated with the redistribution of N from soils to vegetation, the models project a decline in the global vegetation N store, partly related to declining tropical forest biomass. It is worth noting that the N redistribution effect due to climate warming has important implications for the carbon-cycle - climate interaction, which is generally thought to be positive, i.e. amplifying climate change (Gregory et al., 2009). In two studies, which either assumed a closed N cycle with no losses, or had small positive carbon-cycle climate feedback, the response of vegetation growth was strong enough to turn the carbon-cycle - climate interaction into a small negative feedback (Sokolov et al., 2008; Thornton et al., 2009), whereas in another study that described C-N interactions (Zaehle et al., 2010a), the carbon-climate interaction was reduced but remained positive.

The response of the C and N cycles to land-use changes are diverse, and depend on many details of the conversion process, such that it is difficult to establish generic patterns. Converting the land-use type of an ecosystem causes a pronounced disruption of the N cycle, because typically the vegetation N (and C), and sometime fractions of the litter layer and soil organic material, are removed. This causes a phase of reduced vegetation N uptake and enhanced N losses. Forest regrowth is typically associated with an early phase of vigorous tree growth and associated high plant N demands, leading to a conservative N cycle with high N accumulation rates compared to pastures and croplands and consequently reduced N losses (e.g., Davidson et al., 2007). Associated with the forest-to-cropland of grassland-forest conversion are typically declines in soil organic matter stocks (Guo and Gifford, 2002). However, the intricate processes of the N cycle can overrule these trends under particular conditions (Kirschbaum et al., 2008). On a decadal to century time-scale, afforestation and reforestation are therefore typically associated with reduced N_2O emission and N as well as C accumulation, whereas the inverse is true to forest to cropland conversions Davidson et al 2007; Kirschbaum et al., 2013).

Not much is known about the large-scale N cycle consequences of land use change per se, partly owing to the simplistic representation of land use and land use change in most global models (Brovkin et al., 2013). Global model simulations suggest (Fig. 12) that the changes in N storage will largely follow the trends in the C cycle (Zaehle, 2013; Stocker et al., 2013; Brovkin et al., 2013), implying that scenarios will lead to a decline in the vegetation N storage because of the removal of the above-ground vegetation (Fig. 13), and vice versa. Using scenarios in which wide-spread increases in agricultural and pasture areas occur at the expense of forests, global soil C stocks decline with land-use change. However, given that croplands are typically extensively fertilized, the C:N ratio of the soil is often lower, given the higher N content of plant matter, such that the soil retains more N after conversion. The LPX model estimates this conversion effect to be in the order of 2 PgN for the RCP2.6 and 8.5 scenarios (Stocker at al., 2013). These estimates should be treated with due caution, given that these models do not account for a lot of the detailed processes, which affect in particular the change of soil N with time, such as the age-structure and age-dependent development of forests, or the effects of cropland management besides fertilizer additions.

Associated with the projected changes in the terrestrial N and C pools (Fig. 13) are large projected changes in the future net ecosystem N and C balance. Of these fluxes, the change in terrestrial N_2O emission is likely the most climatically relevant factor. Figure 14 shows that projections of the effect of increasing atmospheric CO_2 on the N_2O emissions differ more strongly between models than alternative plausible scenarios of atmospheric CO_2. This difference reflects the large impact of alternative hypotheses about the likely changes of biological N fixation with elevated CO_2, which are large in LPX, but insignificant in the O-CN model. In O-CN, this leads to a progressively more conservative N cycle with reduced N losses, as vegetation growth and N sequestration increases due to CO_2 fertilization. Climate change consistently increases N_2O emissions from terrestrial ecosystem. However, the magnitude of this change is both dependent on the model used (with the LPX model having a higher sensitivity to climate change (Ciais et al., 2013), and the particular climate change scenario. An assessment of the effect of diverging model projections of climate change patterns for a given climate change scenario based on the LPX model revealed large uncertainty in the response of the terrestrial N_2O emissions, which is nonetheless smaller than the differences across alternative climate change scenarios (Stocker et al., 2013). Land use change per se has only little influence on the terrestrial N_2O emissions. However, the historical increase in N fertilizer use has led to a significant increase in the terrestrial N source (Zaehle et al., 2011; Stocker et al., 2013). Importantly, there is a strong interaction between the climate response of terrestrial N_2O emission and N fertilization, as the rate of N_2O production for a given addition of fertilizer increases with climate warming (Butterbach-Bahl and Dannenmann, 2011; Stocker et al., 2013).

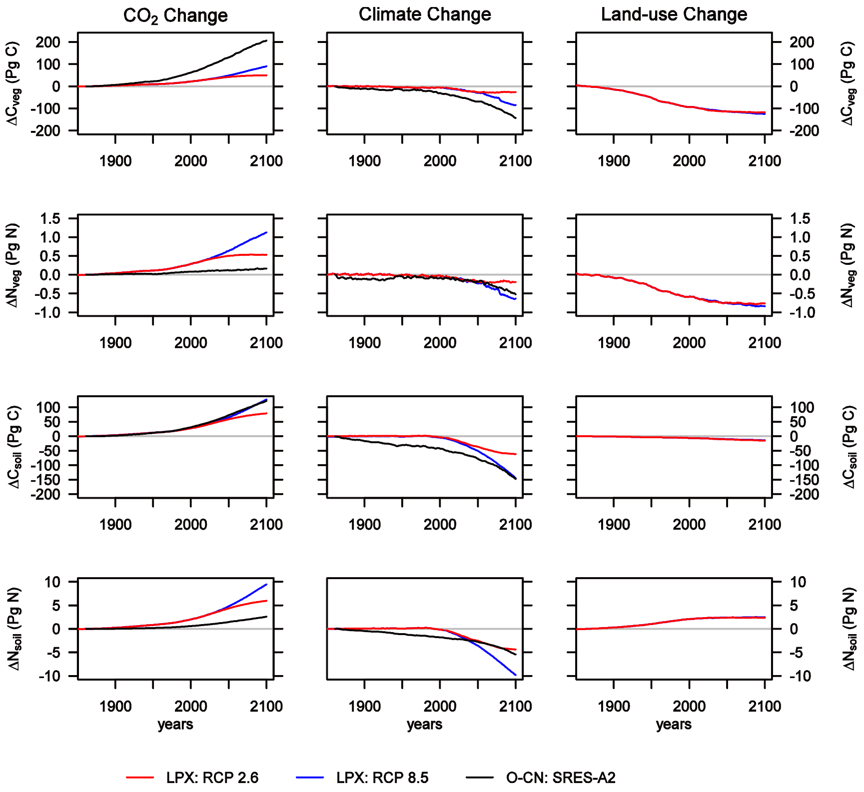

Figure 13: Responses of the terrestrial vegetation and soil C and N pools to projected changes of the atmospheric CO_2 burden, climate, and land-use between 1860 and 2100, as simulated by two global terrestrial biosphere models (LPX, Stocker et al., 2013; and O-CN, Zaehle et al., 2010a). The LPX simulations are based on the climate change projections of HadGEM2-ES model using atmospheric greenhouse gas and land-use forcing for the RCP2.6 and 8.5 scenarios. The O-CN simulations have been driven by climate change projections of the IPSL-CM4 model using the atmospheric greenhouse gas forcing of the SRES-A2 scenario.

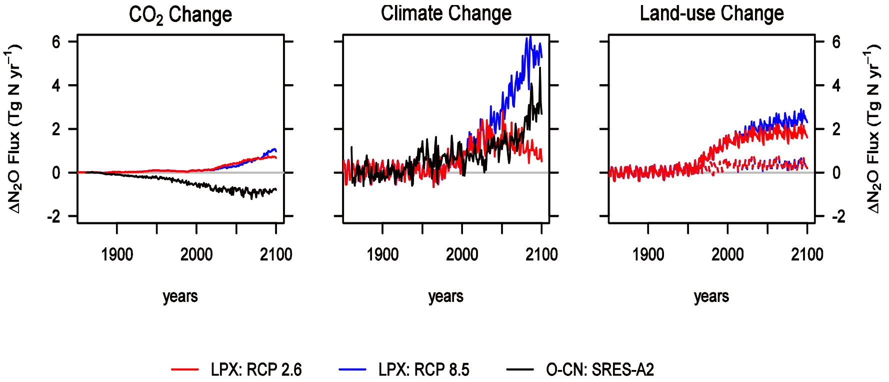

Figure 14: Change in terrestrial N_2O emissions from pre-industrial conditions to projected changes of the atmospheric CO_2 burden, climate, and land-use, as simulated by the two global terrestrial biosphere models (LPX and O-CN), as in Fig. 12. Dashed lines in the land-use change panel refer to projected N_2O emission without the change in fertilizer inputs associated with the RCP scenarios (Stocker et al., 2013).

10 DISCUSSION AND POLICY IMPLICATIONS OF THE RESPONSES OF THE NITROGEN CYCLE TO GLOBAL CHANGE

10.1 Emissions and cycling

The changes in fluxes of N within the global cycle discussed in the main sections of this paper are summarised in Fig. 15. Biological fixation of molecular nitrogen (BNF) is expected to increase during the 21st century both in the oceans (120 to 166 Tg N yr^{-1}) and terrestrial environments (128 to 170 Tg N yr^{-1}) due mainly to changes in climate. Anthropogenic emissions of NH_3 are projected to increase substantially, from 60 to 135 Tg N yr^{-1}. The increase has two components, first the effect of climate, in which higher temperature increase terrestrial emissions and second the effect of increases in N_r fixed by anthropogenic activity in part due to increased demand for food, driven by increases in both global population and changes in diet (especially global meat consumption per capita). By contrast, emissions of combustion related NO_x are projected to decline as the widespread use of control technology (catalytic converters on vehicles and SCR on industrial plant) more than compensate for increases in transport and power production.

The changes in emissions are spatially very variable, reflecting both the current global hotspots of N_r use in Europe, North American and Asia and the expected increases in South and East Asia, Africa and South America where the largest growth in N_r use is expected.

Not all fluxes are projected to be larger at the end of the century, with smaller emissions of NO_x from anthropogenic sources and reduced emission of NH_3 from the oceans (5.7 declining to 1.7 Tg N yr^{-1}) due to the effects of ocean acidification more than compensating the effects of higher water temperatures.

The two large cycles of N_r in terrestrial soils and in the oceans both increase substantially, 240 to 328 Tg N yr^{-1} for soils and 230 to 290 Tg N yr^{-1} in the oceans (Fig. 15).

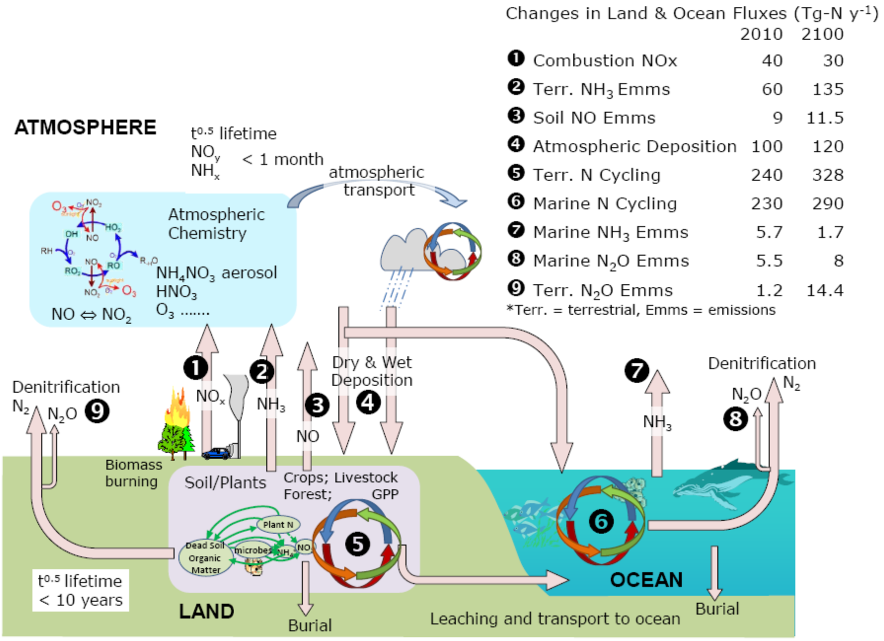

Figure 15: Changes in the major fluxes and in the terrestrial, marine and atmospheric processing of reactive nitrogen (N_r) between 2010 and 2100, adapted from Fowler et al., 2013).

10.2 Effects of changes in atmospheric composition on long range transport of N_r

The removal of sulfur from the atmospheres over Europe and North America has changed the aerosol composition in these regions, with the inorganic aerosol N_r dominated by $(NH_4)_2SO_4$ prior to 1990 and by NH_4NO_3 in more recent years.. Cool season episodes with high particulate matter (PM) concentrations occur widely in Europe in which NH_4NO_3 is a major contributor (Vieno et al., 2014). Likewise in Beijing, NH_4NO_3 is important in winter PM episodes, contributing on average approximately 30% of the PM_{10} mass (Sun et al., 2014). The change in aerosol composition has changed the atmospheric lifetime, deposition footprint and transport distance of much of the emitted reactive nitrogen. Aerosols comprising $(NH_4)_2SO_4$ are largely non-volatile, once formed the aerosol stays in aerosol form until scavenged from the atmosphere by rain. By contrast, NH_4NO_3 is volatile, and close to terrestrial surfaces the deposition of the gaseous HNO_3 and NH_3 to the surface drive the evaporation of the aerosol, especially in warm daytime conditions. These effects increase the atmospheric removal rate of NH_4NO_3 relative to $(NH_4)_2SO_4$ and reduce the lifetime and travel distance of N_r with time during the last 20 years in Europe and North America as the sulfur has been removed from emissions. The trends of increasing importance of NO_3^- aerosols is projected to continue through to the end of this century, with NH_4NO_3 becoming a dominant inorganic component over many regions, despite reductions in NO_x emission due to the increased availability of NH_3 (Hauglustaine et al., 2014). Overall, the changes in atmospheric composition have increased the importance of nitrogen compounds, as a fraction of the pollutant mixture present and in their role in generating effects on ecosystems, human health and climate. One aspect of the likely changes in the characteristics of Nr nitrogen in the environment is the likely changes in the deposition footprint of reactive nitrogen resulting from changes in climate. To date, the effects of climate change on regional patterns of deposition have been explored using regional chemistry-transport models, as described in section 7. The effect on emission –and deposition footprints at the local scale have not, so far been explored even though the principles have been established, of substantially larger emissions of NH_3 (Sutton et al., 2013b) and increased volatilization of aerosol NH_4NO_3 (Nemitz et al., 2014) close to terrestrial surfaces. These changes raise the importance of control measures for emissions of both ammonia and nitrogen oxides and the need for further modelling and field validation of the interactions between reactive nitrogen in the environment and climate.

10.3 Costs

Emissions of N_r from farming activities to the atmosphere, soils and freshwaters are large per unit area relative to the fluxes involved in natural ecosystem BNF and are a substantial contributor to the emission and global N_r deposition hot spots, damage to ecosystems and effects on human health. The processing of N_r in soils and vegetation lead to a wide range of mobile gas and solution phase species and leaks to the wider environment. Only a small fraction (between 20% and 30%) of the N_r used in agriculture is consumed by humans in food (Sutton et al., 2013a), most is wasted either in reactive forms or transformed back to N_2. Current societal costs due to these losses of N_r to the environment are very large. Recent cost-benefit analyses of N_r have been attempted for the Chesapeake Bay in the US (Birch et al., 2011), for Europe (Brink et al., 2011) and as a broad overview for the US (Compton et al., 2011). Table 3 shows the ranges of estimated societal costs per N_r component loss and impact, based on the 'willingness to pay' method for EU27 (Brink et al., 2011). Based on these costs, the most important component of the N_r cycle is the emission of NO_x, due to the human health impacts of both particulate matter and ozone. Sutton et al. (2011) estimated that the agricultural benefits of N_r in Europe are between €10 and €100 billion per year, while the total environmental costs based on the values in Table 3 is in the range €20 and €150 billion per year, making the point that the costs and benefits are of a similar magnitude.

Table 3: Societal costs of nitrogen emissions in ranges based on Brink et al. (2011). Units are euro/kg N_r.

N_r flux	Health	Ecosystem/ coastal systems	crop decline O_3	Climate	Total
NO_x -N to air	10 - 30	2 - 10	1 - 3		13 - 43
NH_3-N to air	1 - 20	2 - 10			3 - 30
N_r to water	0 - 4	5 - 50			5 - 54
N_2O-N to air	1 - 3			1 - 15	2 - 18

10.4 Policies to reduce the impacts of N_r

The overall mass balance for nitrogen compounds is constrained by mass conservation (what goes up must come down), thus the effect of the deposition rate by itself does not change the amount of N_r deposited globally, but the transport distance of the different compounds and regional and importantly the country import/export budgets are changed by changes in chemistry and deposition of the N_r forms present. Only changes to the emissions (and to a lesser denitrification losses to N_2 during atmospheric transport) affect the total N_r amount deposited.

In Europe and the US there are examples of successful policies that led to reduced NO_x emissions, through the Air Quality standards for O_3 and NO_2 in the US and through UN-ECE NO_x and Gothenburg protocols in Europe and large combustion plant directives within the EU. Successful technologies include the three-way catalysts in vehicle exhausts, the Selective Catalytic Converter systems in industry and energy production. Emissions of NO_x declined by 40% in 2009 relative to 1990 in EU27 (EEA, 2012). Policies to reduce NH_3 emission have been much less successful. For NH_3, in the US there are no policies while in Europe the Gothenburg protocol (national NO_x and NH_3 emission ceilings) has led to modest (14%) reductions (EEA, 2012). There are, however, two countries that implemented substantial NH_3 abatement measures and reduced emissions by 40% in Denmark and 50% in the Netherlands. Abatement technologies included: low emission housing systems, coverage of manure storage facilities and application of slurry injection technologies. Furthermore, total N inputs in agriculture were reduced by reducing N in feed and by reducing mineral fertilizer application (Erisman et al., 2005).

The general options of policies to reduce the cascade effect of N_r are:

1. Limit N_r production or limit import of N through animal concentrates
2. Increase N_r use efficiency

3. More evenly distribute N production over the country, over the EU or the world
4. Convert N_r to N_2 catalytically or by stimulating de-nitrification.

Substantial reductions in N_r production by fossil fuels may be achieved by use of renewable energy such as solar, wind and water technologies. The use of biomass as an alternative energy source is not an effective strategy to reduce emissions of N_r (Erisman et al. 2008). Consumer changes in diet and lifestyle present potentially effective measures to reduce emissions, but have proved difficult to implement. Reductions in consumption and therewith production of N_r intensive goods and services offer further valuable control measures that have not been used to date.

Increasing nitrogen use efficiency (NUE) in agricultural systems and by closing nutrient cycles on different scales represents an important guiding principle which has the capacity to deliver both reductions in emission of N_r to the environment and reduced costs in food production. Furthermore as only between 20% and 30% of the nitrogen used in agriculture is concumed by humans, the potential gains in NUE are considerable (MacLeod et al., 2010). The concentration and specialisation of intensive agriculture in certain regionscreates N_r hot-spots, such as in the Netherlands, the North China Plain, (Chen et al., 2014; Shen et al., 2013). In these regions emissions of N_r are visible not just in local measurements, but increasingly from space, using satellite remote sensing (Van Damme et al., 2014). If these agricultural activities were distributed more evenly across the globe, and livestock production located in places where the nutrients are readily available, the N_r losses would be much reduced.

Finally whenever the above options do not prove effective, N_r should be converted back into N_2 by denitrification, to remove N_r from the cascade. Examples of such options include the use of wetlands and waste water treatment plants.

The most effective measures that were selected based on an evaluation of successful policies in the Netherlands were:

- Increasing nitrogen use efficiency in agriculture
- Closing nutrient cycles at different levels
- Influencing consumer behaviour towards reduced meat consumption
- Using technology to reduce emissions from different compartments
- Using spatial planning as a tool to optimise production and environmental protection

In intensive agricultural areas, increasing NUE can be very effective in the short term, whereas in areas with low N inputs closing the nutrient balances is more effective.

Policy instruments are needed to increase NUE. Sutton et al. (2013b) proposed increases in NUE of 20% in agricultural N_r excess areas of the world to reduce the effects of N_r on human health, climate and ecosystems. This would represent a first step to work towards a global policy of nutrient management. However, agricultural subsidies and trade restrictions differ greatly between countries and regions. Such realities distort trade and complicate the introduction of measures designed to promote environmental protection through increases nitrogen use efficiency.

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